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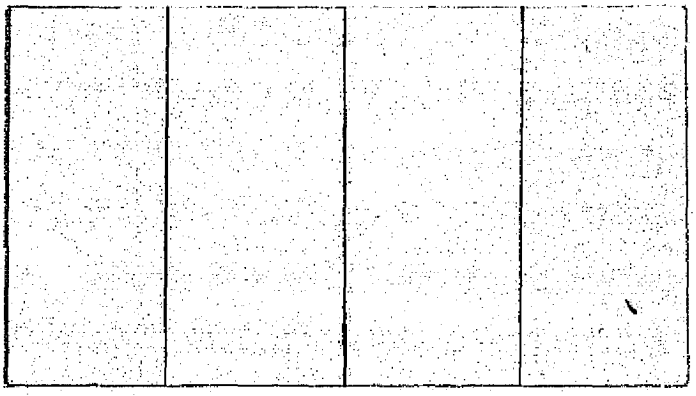

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SURVEY OF HYDROGEN PRODUCTION AND UTILIZATION METHODS

Volume 2. Discussion

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1. INTRODUCTION

Purpose and Objectives

The current energy system is based on naturally available fossil fuels. As domestic supplies of these fuels dwindle and the energy demand continues to grow, more and more fossil fuels are imported. In the long term, the United States may change its energy system to one that is self-sufficient, based on solar, nuclear, and other nonfossil energy sources. The energy from these sources could be used to make electricity or, as has recently been suggested, could be transformed into a synthetic chemical fuel. This project was undertaken to provide the National Aeronautics and Space Administration with technical and economic information on the possibilities of producing and utilizing just such a synthetic energy carrier – hydrogen.

The objectives of this study were –

- To identify and evaluate all developed processes for the production of hydrogen and to assess any novel or unconventional methods discovered during the study
- To review present and potential uses of hydrogen as a fuel, in residential and industrial applications, and as a chemical feedstock
- To prepare recommendations for a series of research projects to develop the technologies needed to bring about a significant use of hydrogen fuel in the United States
- To provide an estimate of the cost of developing these technologies in a broad R&D program planned for the next 5 years.

This report discusses known processes for the production of hydrogen and the present and future industrial uses of hydrogen as a fuel and as a chemical feedstock. Novel and unconventional hydrogen-production techniques have been evaluated, with emphasis placed on thermochemical and electrolytic processes. Potential uses for hydrogen as a fuel in industrial and residential applications were identified and reviewed in the context of anticipated U.S. energy supplies and demands. A detailed plan for the period from 1975 to 1980 has been prepared for research on and development of hydrogen as an energy carrier.

Scope and Definitions

Included in the scope of this study were all hydrogen-production techniques that have been proposed in the literature; studied in laboratories; or operated on a pilot, demonstration-, or commercial-plant scale. Several processes were selected for more detailed study:

- Hydrogen production by electrolysis of pure and impure water
- Thermochemical hydrogen-production processes
- Hydrogen production from coal and water
- Hydrogen production from sunlight and water by photosynthesis or by electrochemical photolysis.

To survey other hydrogen-production processes, the recent literature was was reviewed; and a search was made of U.S patents granted between 1917 and 1974.

The transmission, storage, and delivery of hydrogen were reported on from information presented in the literature. Data on the industrial and residential uses of hydrogen were gathered both from the literature and from interviews conducted with industry representatives. Hydrogen's role in the manufacture of synthetic hydrocarbon fuels was given special attention and is reported on in a separate section.

The use of hydrogen in transportation – whether for automobiles, aircraft, or ships – was specifically excluded from the scope of the study. The potential hydrogen demand by these fuel markets should be kept in mind as the report is reviewed.

To put in context the concept of hydrogen as an energy carrier, this report includes a review of U.S. energy supplies and demands, presented as two energy "models."

Two energy demand and supply projections (models) are detailed – an optimistic possibility of domestic energy self-sufficiency, as well as a pessimistic possibility of continued dependence on energy imports. The projections are not intended to be models of energy allocation; rather, they are intended to show quantitatively the hypothetical deficits and excesses that could exsist in the future. For certain years, the models show energy deficits that must be filled either by imports or by an energy carrier (such as hydrogen) produced from a previously undedicated energy source.

We have chosen to include in this report our survey of industrial hydrogen that is produced "onsite" from feedstocks such as natural gas. Although this "captive" hydrogen may be recombined into another chemical a few minutes after its production, it represents a demand that could be satisfied by synthetic-fuel hydrogen, should it become available at a competitive cost.

In this report, all figures that refer to a quantity of hydrogen as a number of Btu or that cite a hydrogen price in terms of dollars per million Btu are calculated on the basis of gross (or higher) heating value.

2. POTENTIAL DEMANDS FOR HYDROGEN — J. B. Pangborn and J. C. Gillis

Introduction

Two models have been developed to project the U.S. domestic energy demand and supply for the period from 1975 to 2000. These models show the need for development of more conventional and new (unconventional) energy sources and for the conversion of these sources to useful chemical energy and electricity. These hypothetical models are based on assumed growth rates for energy consumption and energy supply. They are intended to delimit the situation that will actually occur in the future in terms of energy deficits and maximum hypothetical demands for hydrogen.

These models do not predict a "most likely" situation, and they are not intended as recommendations for energy allocation. They have been constructed to estimate the bounds of the energy deficits and/or excesses expected for various domestic market sectors. This allows a prediction of the maximum need for alternative fuels (including hydrogen), synthesized from additional or new energy sources, when energy imports from foreign sources are excluded. Hydrogen could be synthesized from either additional conventional energy sources (including nuclear fission) or new energy sources (including solar energy or nuclear fusion).

The premises on which the two models, denoted Model I and Model II, are based are illustrated below. Model I is the "optimistic" case, requiring the least additional energy and the least hydrogen; and Model II is the "pessimistic" case because of the predicted energy deficits and the huge requirements of additional energy.

	Model I	Model II
Energy Supply	IGT post-1973 energy supply projection: high level of supply with synthesized fuels, in the spirit of Project Independence	IGT pre-1973 energy supply projection: moderate level of supply, including some synthesized fuels using coal and oil shale
Energy Demand	NPC "low level" of demand: low rates of economic growth, expensive energy, and energy conservation	NPC "high level" of demand: high rates of economic growth, cheap energy, and little energy conservation

	Model I	Model II
Energy Deficit	Moderate deficits requiring new (more) energy sources and imported energy, large deficits after 1990, complete self-sufficiency unlikely	Extreme deficits requiring huge amounts of new energy and imports, domestic self-sufficiency impossible

Model I Energy Demand and Supply

The assumptions and bases of the energy demand and supply in Model I are presented below. This model determines the lower bound (the least amount) of hydrogen and of additional synthesized fuels and the additional electricity that will be needed, along with imports, to satisfy the U.S. domestic energy demand for the period from 1975 to 2000. We emphasize that these energy requirements are in addition to the synthetic fuel supplies (e.g., SNG) that are projected (optimistically) within the model to be available from coal and oil shale.

Model I Bases and Information Sources

In the future, all market sectors will receive percentages of the total energy supply that differ somewhat from the present percentages. Market-sector-demand growth rates for 1970 to 1985 are patterned after the "low level of demand" presented in the authoritative NPC report for 1973, U.S. Energy Outlook.[7] For this model and during this period, the annual growth in the total energy demand falls from about 3.5% to about 3.3%. We have extrapolated this low-level-demand projection to the year 2000 and have used an average annual growth rate of 2.8% for the period from 1985 to 2000. The growth rates for individual market sectors are listed in Table 2-1. In this model, the electricity-generating sector grows at a rate necessary to adequately supply the other sectors, but this rate does not exceed 5.5%/yr for the supply of electricity to the residential/commercial sector of 6.0%/yr for that to the industrial sector.

Table 2-1. ANNUAL GROWTH RATE OF DEMAND
(Low Level)

Market Sector	1970-1980	1980-1985	1985-2000
	%/yr		
Residential/Commercial	3.0	2.5	2.8
Industrial	2.1	1.9	2.8
Transportation	3.5	3.0	2.8
Other	4.3	5.5	2.8

For this model, the energy supply levels for the future are patterned after two sources: "A Program for Maximizing U.S. Energy Self-Sufficiency" by H. R. Linden[5] and the IGT feasibility study, "Alternative Fuels for Automotive Transportation," performed for the EPA.[8] This is an optimistic model for a future high-level energy supply. It typifies the goals of Project Independence by assuming the rapid development of domestic sources of fossil energy, synthesized fuels, and nuclear power.[6]

Model I Assumptions

The assumptions for Model I include those in respect to —

- Oil supply:

  Oil Supply = Domestic Crude Oil + Condensates + Natural Gas Liquids + Coal Liquids (Hydrocarbons and/or Methanol) After 1980* + Syncrude Products From Oil Shale After 1980

  The transporation sector receives its historic portion, 54.7%, of the oil supply in 1975. After 1975, this market is supplied with all of the shale syncrude plus at least 55% of the remaining oil supply, including coal liquids.

  The residential/commercial sector receives its historic portion of the oil supply, excluding shale oil products. This is 21% of the crude and coal liquids.

  The industrial sector receives its historic portion of the oil supply, excluding shale oil products. This is 17.5% of the crude and coal liquids.

  The other-uses sector receives 0.6% of the supply of crude and coal liquids.

  The electricity-generating sector continues, until 1975, to increase its use of oil. Thereafter, this portion remains constant at 6.2% of the 1975 oil supply. Electricity is produced from oil at a 35% efficiency (delivered).

- Gas supply:

  Gas Supply = Domestic Natural Gas + SNG (Coal-Based) After 1980†

---

* Coal converted to delivered hydrocarbons at a 65% efficiency. Coal converted to delivered methanol at a 45% efficiency.

† Coal converted to delivered SNG at a 65% efficiency from 1980 to 2000.

The residential/commercial sector receives its historic portion, about 32%, of the natural gas in 1975. Because of priorities and allotments, this percentage grows to more than 36% by the year 2000. About one-half of the SNG produced goes to this market.

The industrial sector receives its historic 35.5% of the gas supply.

The electricity-generating sector does not increase its use of gas after 1970. Its historic portion is 17.4% of the 1970 supply. No SNG goes to this market. Electricity is generated from gas at a 35% efficiency (delivered).

The other-uses sector is supplied with about 15% of the natural gas, plus SNG.

The transportation sector uses negligible natural gas and SNG.

- Coal supply (for direct uses, not chemical fuel synthesis). The electricity-generating sector uses its historic 61.9% of the coal supply from 1970 to 1975 and 64.3% of the supply thereafter. Electricity is generated from coal at a 35% efficiency (delivered).

  The industrial sector uses 35.7% of the coal supply (from 1970 to 2000).

  The residential/commercial sector uses 2.3% of the coal supply from 1970 to 1975 and negligible amounts thereafter.

  Negligible coal is used by the transportation and other-uses sectors.

- Electricity consumption. The residential/commercial sector consumes electricity at a rate that grows by 5.5% annually from 1975 to 2000.

  Consumption by the industrial sector grows but the rate does not exceed 6%. (In many years, the demand is not satisfied.)

  The transportation and other-uses sectors consume relatively small amounts of electricity, although the amount consumed by the transportation sector increases rapidly (more than 6%/year).

- Nuclear heat (heat energy, not power). The electricity-generating sector consumes nuclear heat in generating electricity. The electricity demand is determined by the other market sectors. The total nuclear-heat requirement consists of the product electricity (in heat units) plus the waste heat of generation. For purposes of this model, nuclear heat is not used by any other sector, although the model shows that some would be available to other sectors for process uses in fuel synthesis. Electricity is generated from nuclear heat with an efficiency that is at least 35% after 1985.

- Geothermal heat and hydropower. Geothermal heat is used for electricity generation, and it is included with hydropower (as heat) as an energy supply for the electricity-generating sector. In the case of hydropower, of course, waste heat is not significant, and a fuel supply is not required.

- Hydrogen production. In this model, the total supply of fossil fuels, geothermal heat, and hydropower is consumed. However, some potential surplus nuclear heat (not used for electricity generation) does exist. This heat could be used for hydrogen production as follows:

Nuclear heat converted to delivered hydrogen via electrolysis	30% efficient from 1980 to 1985 35% efficient from 1985 to 2000
Nuclear heat converted to delivered hydrogen via thermochemical processes	45% efficient from 1990 to 2000

Model I Overall Demand and Supply Projections

Using the model bases for projections, the energy demands and supplies can be determined by market sector and by type, respectively. We have calculated the market sector demands, and they are presented in Table 2-2. In this table, the electricity-generation demand is the quantity of waste heat resulting from and required in the generation of electricity. The electricity so produced is matched to and included in the projected demands of the other market sectors. The Model I energy supply is presented in Table 2-3.

It should be noted that although the total energy supply numerically exceeds the total demand (by a small amount) after about 1985, this does not imply domestic self-sufficiency, primarily because some of the energy supply, notably the nuclear heat, would be converted to additional useful fuels (or electricity). The associated waste heat is not utilized as a fuel and is in addition to the heat demand listed in Table 2-2 for the electricity-generating sector. This additional waste heat cannot be used to satisfy the demands of the other market sectors; hence, energy (fuel) shortfalls will occur.

Model I Energy Demand and Supply, by Sector

We have used the Model I assumptions to determine the apportionment of domestic energy supplies to the various market sectors: residential/commercial, industrial, transportation, other uses (miscellaneous and nonenergy uses of fuels such as for petrochemical feedstocks, chemical commodities, fertilizers, and lubricants), and electricity generating. The demand and supply projections for these respective market sectors are presented in Tables 2-4 through 2-8. The unfilled demand (the bottom line in Tables 2-4 through 2-7) is the energy deficit to be filled by development of more of the same energy sources than is predicted by the model, exploitation of new energy sources, and energy imports.

Table 2-2. MODEL I ENERGY DEMAND BY MARKET SECTOR

Market Sector	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Residential/Commercial	15.8	18.3	21.1	23.9	27.5	31.6	36.3
Industrial	20.0	22.2	24.7	27.1	31.1	35.7	41.0
Transportation	16.3	19.3	23.0	26.7	30.6	35.1	40.3
Electricity Generating*	11.6	12.8	16.7	18.3	23.4	31.[illegible]	41.6
Other	4.1	5.1	6.2	8.1	9.3	10.8	12.3
Total	67.8	77.7	91.7	104.1	121.9	144.8	171.5

* Matched to electricity demand in other sectors, This is waste heat only.

Table 2-3. MODEL I DOMESTIC ENERGY SUPPLY

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Crude Oil and Condensates	21.0	22.9	27.2	29.6	28.7	26.4	24.3
Natural Gas	22.4	23.5	23.6	26.7	28.5	26.3	24.1
Coal (Direct Use)	13.1	16.0	18.6	21.5	24.9	28.9	33.3
Coal (SNG)	0.0	0.0	1.0	2.0	4.0	6.0	8.0
Coal (Liquids)	0.0	0.0	0.2	1.1	3.7	6.9	10.2
Shale Syncrude	0.0	0.0	0.6	1.9	4.7	5.5	6.7
Hydro- and Geothermal Power (as Heat)	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat	0.2	3.5	9.5	21.0	30.0	42.0	60.0
Total	59.4	68.9	84.2	107.8	129.0	147.0	172.1

Table 2-4. MODEL I RESIDENTIAL AND COMMERCIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	15.8	18.3	21.2	23.9	27.5	31.6	36.3
Fossil-Fuel Supply							
Oil (21% of Crude + Coal Liquids)	4.4	4.8	5.8	6.4	6.8	7.0	7.2
Gas (Available Supply)	7.0	7.6	8.1	10.1	12.0	11.8	11.7
Coal (2.3% of Supply)	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Total Fossil	11.7	12.7	13.9	16.5	18.8	18.8	18.9
Electricity Consumption	2.7	3.2	4.2	5.5	7.2	9.4	12.3
Total Supply	14.4	15.9	18.1	22.0	26.0	28.2	31.2
Unfilled Demand	1.4	2.4	3.1	1.9	1.5	3.4	5.1

Table 2-5. MODEL I INDUSTRIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	20.0	22.2	24.7	27.1	31.1	35.7	41.0
Fossil-Fuel Supply							
Oil (17.5% of Crude + Coal Liquids)	3.7	4.0	4.8	5.4	5.7	5.8	6.0
Gas (35.5% of Supply)	7.9	8.3	8.7	10.2	11.5	11.5	11.4
Coal (35.7% of Supply)	4.7	5.7	6.6	7.7	8.9	10.3	11.9
Total Fossil	16.3	18.0	20.1	23.3	26.1	27.6	29.3
Electricity Consumption	2.3	3.0	4.0	3.8	5.0	6.7	9.0
Total Supply	18.6	21.0	24.1	27.1	31.1	34.3	38.3
Unfilled Demand	1.4	1.2	0.6	0.0	0.0	1.4	2.7

Table 2-6. MODEL I TRANSPORTATION ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	16.3	19.3	23.0	26.7	30.6	35.1	40.3
Fossil-Fuel Supply							
Oil (Shale Syncrude + Balance)	11.5	12.5	15.7	19.2	23.0	24.4	26.3
Gas*		--	--	--	--	--	--
Coal (0.1% of Supply)*	--	--	--	--	--	--	--
Total Fossil	11.5	12.5	15.7	19.2	23.0	24.4	26.3
Electricity Consumption	--*	--*	0.2	0.3	0.4	0.6	0.8
Total Supply	11.5	12.5	15.9	19.5	23.4	25.0	27.1
Unfilled Demand	4.8	6.8	7.1	7.2	7.2	10.1	13.2

* Negligible.

Table 2-7. MODEL I OTHER-USES ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	4.1	5.1	6.2	8.1	9.3	10.8	12.3
Fossil-Fuel Supply							
Oil (0.6% of Supply)	0.1	0.1	0.2	0.2	0.2	0.2	0.3
Gas (15.8% of Supply)	3.5	3.7	3.9	4.5	5.1	5.1	5.1
Coal (0.0% of Supply)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Fossil	3.6	3.8	4.1	4.7	5.3	5.3	5.4
Electricity Consumption*	0.1	0.1	0.2	0.2	0.2	0.3	0.3
Total Supply	3.7	3.9	4.3	4.9	5.5	5.6	5.7
Unfilled Demand	0.4	1.2	1.9	3.2	3.8	5.2	6.6

* Expressed as a constant percentage, 2.5% of the total demand.

Table 2-8. MODEL I ELECTRICITY GENERATION

Demands	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Electricity Produced	5.0	6.3	8.6	9.8	12.8	17.0	22.4
Waste Heat Required	11.3	12.8	16.7	18.3	23.4	31.6	41.6
Total Heat	16.3	19.1	25.3	28.1	36.2	48.6	64.0
Fossil-Fuel Supply							
Oil (6.2% of 1975 Supply)	1.3	1.4	1.4	1.4	1.4	1.4	1.4
Gas (17.4% of 1970 Supply)	3.9	3.9	3.9	3.9	3.9	3.9	3.9
Coal*	8.1	9.9	12.0	13.8	16.0	18.6	21.4
Total Fossil	13.3	15.2	17.3	19.1	21.3	23.9	26.7
Hydro- and Geothermal Power†	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat Required for Remaining Demand	0.3	0.9	4.5	5.0	10.4	19.7	31.8
Total Heat Supply	16.3	19.1	25.3	28.1	36.2	48.6	64.0

* 61.9% of supply from 1970 to 1975, 64.3% thereafter.

† Heat equivalent of hydropower plus heat required for geothermal power.

Model I Demand and Potentials for Hydrogen Production

The demands of the electricity-generating sector, depicted in Table 2-8, do not use all of the potentially available energy supplies: According to the apportionments in this model, some potential excess nuclear heat remains unused. Alternatively (with different model assumptions), some coal could remain unused, instead of this nuclear heat. This nuclear heat is in excess only in the sense that the electricity-generating sector does not need it, and it is potentially available according to the projections used as a basis for Model I. Other sector deficits, summarized in Table 2-9, could be partially filled with a useful fuel generated from this nuclear heat. If this fuel were hydrogen, the potential quantities generated would be as shown in Table 2-9.

Table 2-9. MODEL I MAXIMUM DEMAND AND POTENTIALS FOR HYDROGEN PRODUCTION

	1975	1980	1985	1990	1995	2000
			10^{15} Btu			
Unfilled Demands per Sector*						
Residential/Commercial	2.4	3.0	1.9	1.5	3.4	5.1
Industrial	1.2	0.6	0.0	0.0	1.4	2.7
Transportation (25% of Total Demand for This Sector)	1.7	1.8	1.8	1.9	2.5	3.3
Other	1.2	1.9	3.2	3.8	5.2	6.6
Potential Hydrogen Demand	6.5	7.3	6.9	7.2	12.5	17.7
Unused Nuclear-Heat Supply	2.6	5.0	16.0	19.6	22.3	28.2
Potential Hydrogen Supply (Nuclear Heat)						
Electrolysis	0.0	1.5	4.8	6.1	6.1	6.1
Thermochemical	0.0	0.0	0.0	0.0	1.2	3.9
Total Hydrogen	0.0	1.5	4.8	6.1	7.3	10.0

* Excluding the electricity-generating sector.

Alternatively, of course, the unfilled demands could be satisfied by importing fuels. Because imports are not included in the Model I assumptions for the energy supply, the potentials for hydrogen demand are a maximum case. The minimum case would be zero demand for fuel hydrogen – i.e., complete importation of fuels and feedstocks to satisfy deficits and no need for hydrogen additional to its conventional production from fossil hydrocarbons (especially natural gas). The extent of future importation of energy supplies depends on economic and political factors not assessed in this study.

In Table 2-9, we have summed the shortfalls of the residential/commercial sector, the industrial sector, the other-uses sector, and 25% of the transportation sector to determine the potential demand for hydrogen. Two recent studies on alternative fuels for transportation, conducted for the Environmental Protection Agency, have revealed that before the year 2000 hydrogen will not be among the top three alternative fuels for automotive transportation (cars, trucks, and buses accounting for about 75% of the energy consumption in this sector). Accordingly, only a portion of the transportation

sector shortfall, 25% (for airlines, railroads, and water transport), is a potential market for hydrogen. The potential demand for hydrogen could be satisfied by producing hydrogen from "excess" nuclear heat, from additional fossil resources (i.e., in addition to the supplies listed in Table 2-3), or from "new" energy sources. These new energy sources include solar heat, geothermal heat, waste materials, nuclear fusion, windpower, and ocean thermal gradients.

Model II Energy Demand and Supply

The assumptions and bases for the energy demand and supply in Model II are presented below. These differ from Model I only in the demand-supply data used and in certain assumptions in which Model II data necessitate slight changes. Basically, both models use the same assumptions for energy apportionment. Model II determines the upper bound (the greatest amount) of hydrogen and of additional synthesized fuels and the additional electricity that will be needed, along with imports, to satisfy the U.S. domestic energy demand for the period from 1975 to 2000. As in Model I, imports are not included in the Model II assumptions on energy supply.

Model II Bases and Information Sources

In the future, all market sectors will receive percentages of the total energy supply that differ somewhat from the present percentages. Market-sector-demand growth rates for 1970 to 1985 are patterned after the "high level of demand" presented in the authoritative NPC report for 1973, U.S. Energy Outlook.[7] For this model and during this period, the annual growth in the total energy demand falls from about 4.5% to about 4.3%. We have extrapolated this high-level-demand projection to the year 2000 and have used an average annual growth rate of 3.8% for the period from 1985 to 2000. The growth rates for individual market sectors are given in Table 2-10. The electricity-generating sector grows at a rate necessary to adequately supply the other sectors, but this rate does not exceed 7.0%/yr for supply of electricity to the residential/commercial sector or 7.5% for that to the industrial sector.

In Model II, the energy supply levels for the future are patterned after the pre-1973 projections included in the study, "A Program for Maximizing U.S. Energy Self-Sufficiency," by H. R. Linden.[5] Presented in this study,

Table 2-10. ANNUAL GROWTH RATE OF DEMAND
(High Level)

Market Sector	1970-1980	1980-1985	1985-2000
	%/yr		
Residential/Commercial	4.0	4.0	3.8
Industrial	3.1	3.2	3.8
Transportation	4.1	3.5	3.8
Other	5.3	6.2	3.8

in addition to the case used in Model I, is a less optimistic projection of the energy supply, and this case corresponds to the energy economics prevailing before the 1973 Middle East oil embargo. Reasonable development of domestic natural resources and growth of a synthetic fuel industry are assumed. Large amounts of imported energy are necessary for a demand-supply balance, and the domestic energy supply is necessarily less than that in Model I.

The energy-demand levels are the "high levels" presented in the NPC study, U.S. Energy Outlook.[7] The effect of energy conservation in the United States is assumed insignificant (at least from 1975 to 1985); and the demand growth rates continue at high levels, similar to those prevailing before the "energy crisis" began. However, these demand growth rates (except that for electricity) do decrease with time.

Model II Assumptions

The assumptions for Model II include those in respect to —

- Oil supply:

  Oil Supply = Domestic Crude Oil + Condensates + Natural Gas Liquids + Coal Liquids After 1985* + Syncrude Products From Oil Shale After 1980.

  The distribution of the oil supply in Model II follows the same pattern as that in Model I.

- Gas supply:

  Gas Supply = Domestic Natural Gas + SNG (Coal-Based) After 1980†

* Coal converted to delivered hydrocarbons at a 65% efficiency from 1985 to 2000.

† Coal converted to delivered SNG at a 65% efficiency from 1980 to 2000.

In Model II, the electricity-generating sector receives its historic portion, 17.4%, of the natural gas supply (a variable quantity). This is less gas than in Model I, in which this sector continues to receive the fixed quantity of 17.4% of the 1970 supply. Otherwise, the distribution of the gas supply follows the same pattern as that in Model I. This minor change makes slightly more of the limited supply of natural gas available to higher priority market sectors.

- Coal supply (for direct uses, not chemical fuel synthesis). The distribution of the coal supply in Model II follows the same pattern as that in Model I.

- Electricity consumption. The residential/commercial sector consumes electricty at a rate that grows 7.0% annually from 1975 to 2000. Consumption by the industrial sector grows but it does not exceed 7.5%. (In many years, the demand is not satisfied.)

  The transportation and other-uses sectors consume relatively small amounts of electricity, although the amount consumed by the transportation sector increases rapidly (more than 6%/year).

- Nuclear heat, geothermal heat, and hydropower. The distribution of these energy sources in Model II follows the same pattern as that in Model I.

- Hydrogen production. In Model II, the total supply of fossil fuels, geothermal heat, and hydropower is consumed. Relatively small amounts of nuclear heat, potentially in excess of the needs of the electricity-generating sector, would exist from 1975 to 1990. Otherwise, there are nuclear energy deficits. Because of the small nuclear-heat supply and the 15-year time period, a hydrogen-production industry in this model would require significant energy sources other than nuclear fission reactors. For the nuclear (fission) heat that is available, we have assumed the following conversion efficiencies:

Nuclear heat converted to delivered hydrogen via electrolysis	30% efficient from 1980 to 1985 35% efficient from 1985 to 1990

  No thermochemical hydrogen processes based on nuclear (fission) heat will be commercialized because, according to this model, required nuclear heat will not be available after 1990. Thermochemical processes based on new energy sources could be commercialized.

Model II Overall Demand and Supply Projections

As in Model I, we have used the model bases to tabulate the energy demands by market sector and the energy supplies by type. These are presented in Tables 2-11 and 2-12, respectively. The demand of the electricity-generating sector is waste heat only, as in Model I. This prevents double counting of the electricity demand for each market sector.

Table 2-11. MODEL II ENERGY DEMAND BY MARKET SECTOR

Market Sector	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Residential/Commercial	15.8	19.2	23.4	28.5	34.3	41.3	47.9
Industrial	20.0	23.8	27.2	31.9	38.4	46.3	55.8
Transportation	16.3	19.9	24.4	29.0	34.9	42.1	50.7
Electricity-Generating*	11.6	13.2	18.2	24.6	34.2	49.1	69.3
Other	4.1	5.3	6.8	9.2	11.1	13.4	16.1
Total	67.8	81.4	100.0	123.2	152.9	192.2	239.8

* Matched to electricity demands in other sectors assuming certain conversion efficiencies. This is waste heat only.

Table 2-12. MODEL II DOMESTIC ENERGY SUPPLY

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Crude Oil and Condensates	21.0	21.9	24.3	23.9	24.3	22.7	22.9
Natural Gas	22.4	21.2	18.8	17.6	17.1	16.9	16.7
Coal (Direct Use)	13.1	16.0	18.6	21.5	24.9	28.9	33.3
Coal (SNG)	0.0	0.0	0.2	1.1	3.3	6.0	8.5
Coal (Liquids)	0.0	0.0	0.0	0.4	2.4	5.2	8.2
Shale Syncrude	0.0	0.0	0.2	0.6	2.5	4.5	6.4
Hydro- and Geothermal Power (as Heat)	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat	0.2	3.5	9.5	21.0	30.0	42.0	60.0
Total	59.4	65.6	75.1	90.1	109.0	131.2	161.5

Because of the bases used, the total energy demand and the domestic energy supply are badly out of balance in Model II. New, large-scale energy sources and imports would be required to meet the demands in this model.

Model II Energy Demand and Supply, by Sector

Here, as in Model I, we have used the assumptions to determine the apportionment of domestic energy supplies to the various market sectors. The demand and supply projections for these market sectors are presented in Tables 2-13 through 2-17. The unfilled demand (the bottom line in Tables 2-13 through 2-16) is the energy deficit to be filled by development of more of the same energy sources than is predicted by the model, exploitation of new energy sources, and energy imports.

Table 2-13. MODEL II RESIDENTIAL AND COMMERCIAL ENERGY DEMAND AND SUPPLY
(Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	15.8	19.2	23.4	28.5	34.3	41.3	47.9
Fossil-Fuel Supply							
Oil (21% Crude and Coal Liquids)	4.4	4.6	5.1	5.1	5.6	5.9	6.5
Gas (Available Supply)	7.0	6.7	6.0	6.0	7.0	8.2	9.4
Coal (2.3% of Supply)	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Total	11.7	11.6	11.1	11.1	12.6	14.1	15.9
Electricity Consumption	2.7	3.3	4.6	6.4	9.0	12.6	17.6
Total Supply	14.4	14.9	15.7	17.5	21.6	26.7	33.5
Unfilled Demand	1.4	4.3	7.7	11.0	12.7	14.6	14.4

Model II Demand and Potentials for Hydrogen Production

The demands of the electricity-generating sector, depicted in Table 2-17, do not require all of the available energy supplies for the years 1975 to 1990. Potentially, relatively small amounts of excess nuclear heat exist during this

Table 2-14. MODEL II INDUSTRIAL ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	20.0	23.8	27.2	31.9	38.4	46.3	55.8
Fossil-Fuel Supply							
Oil (17.5% of Crude and Coal Liquids)	3.7	3.8	4.2	4.3	4.7	4.9	5.4
Gas (35.5% of Supply)	7.9	7.5	6.7	6.6	7.2	8.1	8.9
Coal (35.7% of Supply)	4.7	5.7	6.6	7.7	8.9	10.3	11.9
Total Fossil	16.3	17.0	17.5	18.6	20.8	23.3	26.2
Electricity Consumption	2.3	3.1	4.4	6.3	9.0	12.9	18.5
Total Supply	18.6	20.1	21.9	24.9	29.8	36.2	44.7
Unfilled Demand	1.4	3.7	5.3	7.0	8.6	10.1	11.1

Table 2-15. MODEL II TRANSPORTATION ENERGY DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	16.3	19.9	24.4	29.0	34.9	42.1	50.7
Fossil-Fuel Supply							
Oil (Shale Syncrude and Balance)	11.5	12.0	13.7	14.0	17.3	20.0	24.0
Gas*	--	--	--	--	--	--	--
Coal (0.1% of Supply)	--	--	--	--	--	--	--
Total Fossil	11.5	12.0	13.7	14.0	17.3	20.0	24.0
Electricity Consumption	--	--	0.2	0.3	0.4	0.6	0.8
Total Supply	11.5	12.0	13.9	14.3	17.7	20.6	24.8
Unfilled Demand	4.8	7.9	10.5	14.7	17.2	21.5	25.9

* Negligible.

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Table 2-16. MODEL II OTHER USES OF FUELS DEMAND AND SUPPLY (Domestic)

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demand	4.1	5.3	6.8	9.2	11.1	13.4	16.1
Fossil Fuel Supply							
Oil (0.6% of Crude and Coal Liquids)	0.1	0.1	0.1	0.1	0.2	0.2	0.2
Gas (15.8% of Supply)	3.5	3.3	3.0	3.0	3.2	3.6	4.0
Coal*	--	--	--	--	--	--	--
Total Fossil	3.6	3.4	3.1	3.1	3.4	3.8	4.2
Electricity Consumption†	0.1	0.1	0.2	0.2	0.3	0.3	0.4
Total Supply	3.7	3.5	3.3	3.3	3.7	4.1	4.6
Unfilled Demand	0.4	1.8	3.5	5.9	7.4	9.3	11.5

*Negligible.

†Expressed as a constant percentage, 2.5%, of the total demand.

Table 2-17. MODEL II ELECTRICITY GENERATION

	1970	1975	1980	1985	1990	1995	2000
	10^{15} Btu						
Demands							
Electricity Produced	5.0	6.5	9.4	13.2	18.7	26.4	37.3
Waste Heat Required	11.3	13.2	18.2	24.6	34.2	49.1	69.3
Total Demand	16.3	19.7	27.6	37.8	52.9	75.5	106.6
Fossil-Fuel Supply							
Oil (6.2% of 1975 Supply)	1.3	1.4	1.4	1.4	1.4	1.4	1.4
Gas (17.4% of N.G. Supply)	3.9	3.7	3.3	3.1	3.0	3.0	2.9
Coal (61.9% of Supply, 64.3% after 1975)	8.1	9.9	12.0	13.8	16.0	18.6	21.4
Total Fossil	13.3	15.0	16.7	18.3	20.4	23.0	25.7
Hydro- and Geothermal Power*	2.7	3.0	3.5	4.0	4.5	5.0	5.5
Nuclear Heat Required for Remaining Demand	0.3	1.7	7.4	15.5	28.0	47.5	75.4
(Nuclear Heat Available†)	(0.3)	(3.5)	(9.5)	(21.0)	(30.0)	(42.0)	(60.0)
Total Heat Supply	16.3	19.7	27.6	37.8	52.9	70.0	91.2

*Heat required for generation.

†Not included in total.

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period. However, after 1990 there is a shortfall in the energy supply for this sector. According to the assumptions of Model II, the excesses and deficits are nuclear heat; but with different assumptions, these quantities could be expressed as coal energy.

Table 2-18 lists the individual energy shortfalls for each sector and the quantities of hydrogen that are potentially available from the excess nuclear heat. As in Model I, we have calculated the potential demand for hydrogen by summing up the sector deficits (using 25% of the transportation-sector deficit). Although the electricity-generating sector has energy deficits in Model II, we have excluded its demand from the total potential hydrogen demand because it is not considered practical to synthesize hydrogen for use as a fuel to generate electricity. The reasons for this are the large required hydrogen capacity and the capital costs that result from the accumulative energy losses associated with the many consecutive energy-conversion steps.

Table 2-18. MODEL II MAXIMUM DEMAND AND POTENTIALS FOR HYDROGEN PRODUCTION

	1975	1980	1985	1990	1995	2000
	10^{15} Btu					
Unfilled Demands by Sector*						
Residential/Commercial	4.3	7.7	11.0	12.7	14.6	14.4
Industrial	3.7	5.3	7.0	8.6	10.1	11.1
Transportation	7.9	10.5	14.7	17.2	21.5	25.9
Other	1.8	3.5	5.9	7.4	9.3	11.5
Potential Hydrogen Demand	11.8	19.1	27.6	33.0	39.4	43.5
Unused Nuclear Heat Supply	1.8	2.1	5.5	2.0	0.0†	0.0†
Potential Hydrogen Supply (Nuclear Heat)						
Electrolysis	0.0	0.6	1.6	0.7	0.0	0.0

* Excluding the electricity.

† Actually a deficit.

The potential demand for hydrogen might be satisfied by producing hydrogen from potential excess nuclear heat, from additional fossil resources (i.e., in addition to the supplies listed in Table 2-12), or from new energy sources. These new energy sources include solar heat, waste materials, nuclear fusion, windpower, and ocean thermal gradients. As is the case with Model I, the sector deficits here also might be filled by energy imports. As this model does not include imports, the deficits and the attendant hydrogen demands constitute a maximum case for hydrogen demand.

Summary of Potential Hydrogen Demand

The potential maximum demand for hydrogen is bracketed by using the sector demands (for hydrogen) from each model. The lower bound is the value from Model I, and the upper bound is the value from Model II. We stress that this potential demand could be filled by hydrogen, or by combinations of hydrogen with other synthesized chemical fuels and electricity. Imported energy could also contribute. If domestic energy were to supplement, new and additional energy sources, beyond those included in the models, would be necessary. Assuming, however, that these demands are met solely by hydrogen, then the bounds of the potential hydrogen demand are as presented in Table 2-19.

Table 2-19. BOUNDS OF POTENTIAL MAXIMUM DEMAND FOR HYDROGEN

Market Sector	1975	1980	1985	1990	1995	2000
	10^{15} Btu					
Residential/ Commercial	2.4- 4.3	3.0- 7.7	1.9-11.0	1.5-12.7	3.4-14.6	5.1-14.4
Industrial	1.2- 3.7	0.6- 5.3	0.0- 7.0	0.0- 8.6	1.4-10.1	2.7-11.1
Transportation	1.7- 2.0	1.8- 2.6	1.8- 3.7	1.9- 4.3	2.5- 5.4	3.3- 6.5
Other	1.2- 1.8	1.9- 3.5	3.2- 5.9	3.8- 7.4	5.2- 9.3	6.6-11.5
Total	6.5-11.8	7.3-19.1	6.9-27.6	7.2-33.0	12.5-39.4	17.7-43.5

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Present and Future Demands for Specific Uses of Hydrogen

Models I and II show the limits of the size of the "energy gap" that could be filled by a fuel such as hydrogen. Examination of these two models is useful because it shows that the traditional supplies of domestic energy

will be unable to satisfy a large portion of the future energy market; thus there is an opening for a new energy carrier such as hydrogen. In addition, one model shows that some nuclear heat, up to 28.2 quadrillion Btu in the year 2000, could potentially be available for hydrogen synthesis. The question that remains is: In what fashion could the synthesized hydrogen be utilized?

We have surveyed portions of the market for present and future uses of hydrogen to show how some of the "energy gaps" predicted by Models I and II might be filled by hydrogen. The market estimates are not comprehensive, are not taken directly from either Model I or Model II, and should not be compared directly to them without expecting some incongruities. Instead, the estimates are based on the extrapolation of historical data, and model growth rates are used only when necessary.

Extrapolation of Present-Day Hydrogen Demands

Table 2-20 shows the largest present-day uses of hydrogen (as a feedstock or intermediate), the amount of hydrogen so consumed in 1973, and their growth rates, as given by various sources.

Table 2-20. PRESENT-DAY HYDROGEN USES AND GROWTH RATES

Use	1973 Usage, 10^{15} Btu	Annual Growth Rate, %
Ammonia Synthesis[9]	0.340*	4.5
Chemical Methanol Synthesis[2]	0.076*	6.0
Oil Refining[1]		
Hydrotreating	0.176	10.0
Hydrocracking	0.241	<1.0
Others[9]	0.049*	10.0

* U.S. Bureau of Mines, "Hydrogen Commodity Statement 1973," unpublished. Washington, D. C., December 1974.

To estimate the demand for hydrogen from these sources, we have made the following assumptions:

- Ammonia and chemical methanol synthesis will grow at their historical rates.

- Because of recently applied sulfur restrictions, hydrotreating is growing at an accelerated rate. This rate was assumed to continue until 1979, at which point the hydrotreating growth rate would decrease to that of oil refining in general.
- The growth of hydrocracking is currently depressed, primarily by the sudden shortage of natural gas. It is assumed that hydrocracking will begin to grow again at the same rate as oil refining in general, in 1980.
- The rate of growth for oil refining was assumed to be about 2% per year, (as indicated by Model II).
- The "other" uses of hydrogen have been growing at a rate of 10% per year. It was assumed that this growth rate would continue until 1985, then decrease to a rate of 5% per year after that.

Table 2-21 thus shows the estimated hydrogen demand for traditional uses (feedstock or intermediate that could become a feedstock).

Table 2-21. HYDROGEN DEMAND FOR TRADITIONAL USES

Use	1973	1980	1985	1990	1995	2000
	10^{15} Btu/yr					
Ammonia Synthesis	0.340	0.46	0.60	0.7	0.9	1.1
Chemical Methanol Synthesis	0.076	0.11	0.15	0.20	0.30	0.4
Oil Refining						
Hydrotreating	0.176	0.34	0.38	0.41	0.46	0.5
Hydrocracking	0.241	0.26	0.29	0.32	0.35	0.4
Other	0.049	0.10	0.15	0.20	0.25	0.3
Total	0.882	1.27	1.57	1.83	2.26	2.7

Future Uses of Hydrogen as a Chemical Feedstock

In the next few decades, a number of new markets for hydrogen may open up. Hydrogen may be used as a reducing gas in iron ore refining, and estimates have been published showing the quantities of hydrogen that may thus be needed. Table 2-22 gives the estimates of hydrogen usage presented in a report[3] by The Futures Group.

As will be shown in a later section of this report, tremendous amounts of hydrogen will be needed for coal liquefaction and gasification processes. Oil shale processing, while less hydrogen intensive than the production of clean fuels from coal, will also require large amounts of hydrogen. Table 2-23 shows, for each process, the approximate quantity of hydrogen needed per

Table 2-22. DEMAND FOR HYDROGEN BY IRON ORE DIRECT-REDUCTION PROCESSES

Year	Demand, 10^{15} Btu/yr
1980	0.102
1985	0.215
1990	0.357
1995*	0.487
2000	0.650

*Interpolated.

Table 2-23. HYDROGEN DEMAND FOR SYNTHETIC FUEL PROCESSES PER UNIT OF OUTPUT

Process	Demand, SCF of Hydrogen
Coal Gasification	1.3/SCF of methane
Coal Liquefaction	6000/bbl of syncrude
Oil Shale	1100/bbl of 45° API-gravity syncrude

unit of product. These hydrogen demands were calculated from process flow sheets and represent the amount of molecular hydrogen utilized in each process. Hydrogen generated in a process in a manner such that an outside stream of hydrogen could not be substituted for it is not counted. Table 2-24 shows the demand for hydrogen that would be created if the if the synthetic-fuels industry were to grow at the rate predicted by Model II.

Table 2-24. HYDROGEN DEMAND FOR SYNTHETIC FUEL PROCESSES (Model II Growth)

Process	1980	1985	1990	1995	2000
			10^{15} Btu/yr		
Coal Gasification	0.09	0.48	1.45	2.65	3.74
Coal Liquefaction	0.00	0.14	0.84	1.81	2.86
Oil Shale	0.01	0.04	0.16	0.29	0.41
	0.10	0.66	2.45	4.75	7.01

Hydrogen as a Substitute for Natural Gas

Hydrogen may be very useful as a supplementary or gaseous fuel. To estimate this demand, we have used the projections given in "Future Gas Consumption of the United States," by the Future Requirements Committee (FRC) of the American Gas Association.[4] This publication presents expectations for the gaseous-fuel market during this century if supply were not a problem.

Table 2-25 shows the gas supply predicted by Model II, the demand estimated by the FRC (excluding all interruptible supplies), and the unfilled demand (the difference between the two amounts).

Table 2-25. GASEOUS FUEL SUPPLY AND DEMAND

	1980	1985	1990	1995	2000*
	10^{15} Btu/yr				
Demand (FRC)	25.3	30.1	34.9	41.6	49.2
Supply (Model II)	20.0	18.7	20.4	22.9	25.2
Unfilled Demand	5.3	11.4	14.5	18.7	24.0

* Extrapolated.

It should be clear from Table 2-21, 2-22, 2-24, and 2-25 that, although there are sizable demands for hydrogen as a chemical, the largest market for hydrogen will be its use as a fuel – if it can be produced and delivered cheaply.

References Cited in This Section

1. Aalund, L. R., "Refining Capacity Registers Largest Nickel and Dime Jump in History," Oil Gas J. 72, 76-79 (1974) April 1.

2. "Chemical Profile...Methanol," Chem. Mark. Rep. 205, 9 (1974) June 17.

3. Fein, E., "A Hydrogen-Based Energy Economy," Rep. No. 69-08-10 for Northeast Utilities. Glastonbury, Conn.: The Futures Group, October 1972.

4. Future Requirements Committee, "Future Gas Consumption of the United States," Vol. 5. Denver: Denver Research Institute, November 1973.

5. Linden, H. R., "A Program for Maximizing U.S. Energy Self-Sufficiency," Chicago: Institute of Gas Technology, March 1974.

6. Linden, H. R., "The Role of Gas in 'Project Independence,'" (as presented at the Southern Gas Association Annual Convention). Chicago: Institute of Gas Technology, April 1974.

7. National Petroleum Council, U.S. Energy Outlook: A Report of the National Petroleum Council's Committee on the U.S. Energy Outlook. Washington, D.C., December 1972.

8. Pangborn, J. and Gillis, J., "Alternative Fuels for Automotive Transportation — a Feasibility Study," EPA-460/3-74-012b. Ann Arbor: U.S. Environmental Protection Agency, July 1974.

9. U.S. Department of Commerce, "Industrial Gases — 1973," Curr. Ind. Rep. Ser. M28C(73)-14. Washington, D.C.: Bureau of the Census, August 1974.

3. HYDROGEN PRODUCTION BY ELECTROLYSIS – D. P. Gregory

Introduction

The production of hydrogen by the electrolysis of water is, in principle, very simple. The basic electrolysis cell consists of a pair of electrodes immersed in a conducting electrolyte dissolved in water. A direct current is passed through the cell from one electrode to the other. Hydrogen is evolved at one electrode, oxygen is evolved at the other, and water is thus removed from the solution. In a continuously operating electrolysis cell, replacement of the pure water is continuously supplied; and a continuous stream of hydrogen and oxygen may be obtained from the two electrodes. In practice, electrolysis cells are rather more complicated than this, containing various other components that allow them to work efficiently and economically. Because the basic electrolysis cell has no moving parts, it is reliable and trouble-free; and electrolysis represents the least labor-intensive method of producing hydrogen. In addition to the trouble-free operation, electrolysis is the most efficient way of generating hydrogen under pressure. Increasing the pressure of operation of the cell results in a higher theoretical voltage requirement to drive the cell, but electrolysis cells normally work more efficiently at a higher pressure; and the gain in efficiency usually more than offsets the extra electrical energy requirement.

The most important characteristic of electrolysis is not that hydrogen and oxygen are split out from water, but that they are separated at the same time. This benefit is derived at the expense of having to use a high "energy form," namely electric power, as the input to the cell. Electrolysis has traditionally been considered one of the more expensive methods of hydrogen production and electrolyzers have been assumed to be inefficient and expensive. On the contrary, it is the electric-generation step that is expensive and inefficient; and most commercial electrolyzers available today are capable of operating at electricity-to-hydrogen efficiencies above 75%, while their capital-cost potential is far less than that of the power stations that would be required to run them.

In this section, the principles of electrolysis and the energy requirements for production of electrolytic hydrogen are discussed. The various basic designs of electrolyzer cells are described, as are some of the available

units. The status of industrial electrolytic hydrogen production is such that this method represents only a small fraction of the total hydrogen-production capacity, but a large number of small electrolysis plants exist in various parts of the world; and the location and size of some of the larger ones are described in this report. The estimated costs of hydrogen produced by various electrolyzers as a function of electric power costs have been calculated and an outline of various research programs, largely aimed at reducing the cost of electrolytic hydrogen production, is given.

Principles of Electrolysis

When a direct current is passed through water between two electrodes, water decomposes according to the reaction –

$$H_2O \rightarrow H_2 + {}^1/_2 O_2$$

Water is actually a poor conductor of electricity; and in order for this reaction to proceed, a conducting electrolyte must be added to the water. Water essentially dissociates into hydrogen and hydroxyl ions (H^+ and OH^-). The positive hydrogen ions migrate toward the cathode, the negative electrode, where they are discharged by picking up electrons and forming hydrogen molecules:

$$2H^+ + 2e^- \rightarrow H_2$$

The hydrogen molecules accumulate on the surface of the electrode until a bubble forms, breaks away, and rises to the surface of the electrolyte. At the oxygen electrode, a similar process occurs in which hydroxyl ions are discharged by giving up their electrons to the electrode and reacting to form water and oxygen. The oxygen molecules accumulate into gas bubbles and rise to the surface.

Both of these electrode reactions require some intermediate catalytic reaction with a metal surface. It is believed that the hydrogen ions discharge on the metal surface to form an adsorbed layer of hydrogen atoms, which then recombine on the surface to form hydrogen molecules. The ease with which the electrode reactions occur is profoundly affected by both the physical and chemical natures of the surfaces of the electrodes.

A basic electrolyzer cell consists of the following components:

- An electrolyte – a water solution made conductive by mixing a salt or compound with water. The selection of the electrolyte is important because it must have the following characteristics: It must exhibit high

ionic conductivity; it must not be chemically decomposed by voltage as large as that applied to the cell (so that only water is decomposed); it must not be volatile enough to be removed with the evolved gas; and, because hydrogen-ion concentrations are being rapidly perturbed at the electrodes, the electrolyte should have a strong resistance to pH changes – i.e., it should be a buffer solution.

For the most practical applications, these criteria can be met by the use of a strong acid, such as sulfuric acid, or a strong alkali, such as potassium hydroxide (KOH). Most salts are themselves decomposed under electrolysis at voltages likely to be encountered in an electrolyzer cell. Acid electrolytes present severe corrosion problems and are not usually selected for electrolyzers. Therefore, most commercial electrolyzers operate with an alkaline electrolyte. Maximum conductivity occurs in KOH solutions at about a 30% concentration, and this is the concentration usually selected. There is one notable exception to this use of alkaline electrolytes – the use of a solid polymeric ion-exchange material that also has good ionic conductivity. Ion-exchange resins having mobile negative ions (in other words, alkaline ion-exchange resins) are notoriously sensitive to chemical degradation at elevated temperatures, and this restricts the choice of ion-exchange electrolytes to acidic systems. The most successful work with ion-exchange electrolytes has been carried out using a polymerized fluorinated polystyrene sulfonic acid.

- Electrodes that have the following characteristics – they must be electronic conductors; they must have a suitable catalytic surface for the discharge of hydrogen or hydroxyl ions; they must provide a large-area interface between the catalyst and the electrolyte; they must provide adequate sites for the nucleation of gas bubbles; and they must provide a reasonable means for the detachment of gas bubbles so that they may separate themselves from the electrolyte at the operating voltage of the cell.

  The form of the electrodes varies considerably from one cell design to another. Large surface areas are obtained by the use of sintered structures, finned bodys, screens, perforated plates, and flat plates with electrochemically roughened surfaces. In the alkaline cells, nickel is the most commonly used catalytic surface. Rather than making electrodes out of solid nickel, nickel-plated mild steel is often used. The application of precious-metal catalysts, such as platinum, assists the electrode processes considerably and allows them to proceed more rapidly than on nickel, but the extra cost of the precious metal is not usually considered justified. In the case of the polymeric acid electrolyte, electrodes must be made of more chemically resistant materials than nickel or steel. Tantalum and gold have been used, while the precious metals themselves, platinum, rhodium, iridium, etc., are usually considered necessary as catalysts. When platinum is used, a large surface area can be obtained by the use of so-called platinum black, a finely divided powder of platinum metal particles.

- A separator – required between the two electrodes and serving the following purposes: It prevents the electrodes from touching each other and shorting out, and it prevents the hydrogen and oxygen gases from mixing together inside the cell. To provide this function properly, the separator must consist of a porous diaphragm or matrix through which the electrolyte solution can pass, affording an ionic conducting path from one side of the cell to the other. These pores must remain full of liquid so that gas cannot penetrate them. Additionally, the separator material must not be corroded by the electrolyte in the presence of hydrogen or oxygen gas, and it must remain structurally stable for the entire operating life of the cell so that the pores do not collapse. To keep the ionic resistance of the cell as low as possible, the separator is usually made in the form of a thin sheet, the thickness of which is determined by mechanical strength and gas crossover limitations. In the case of alkaline cells, asbestos has commonly been used for the separator material. Woven asbestos cloth and matted asbestos fibers are both used in commercial cells. Some experimental materials, including potassium titanate, have been used in other alkaline cells. In the case of the polymeric acid ion-exchange resin, this material acts as its own separator; and no additional material is needed.

- A container – required to hold the electrolyte. In some cells, a nickel-plated steel tank with a lid is used, while in others, solid metal sheets are interposed between the electrodes, which are then stacked together with peripheral gaskets used to seal the outer edges. This way, no separate container is required, and current is passed from one electrode to the next through the metal separator plate.

In addition to the basic components of the electrolyzer cell itself, an electrolyzer "system" requires further components. These include power-conditioning equipment to convert ac power to the dc current required by the cell; electrical bus bar equipment to distribute the dc power to the various electrodes in an assembly of electrolyzer cells; gas-exit pipe work to duct the hydrogen and oxygen away from the cell; separation systems to separate the gases from the electrolyte, which may be entrained with the gas or deliberately circulated out of the cell with the gas; cooling systems to remove waste heat from the cell itself; and drying systems to dry the hydrogen and oxygen after they have been generated. Thus, an electrolyzer system may be seen to be far more complex than the simple concept of "two electrodes in an electrolyte" that was presented earlier. Later in this section, options for electrolyzer cell and system designs will be described and discussed in more detail.

Energy Requirements for Electrolysis

The overall process of water decomposition by electrolysis is the reverse of the process of hydrogen combustion. Therefore, the theoretical amount of

energy required per unit quantity of hydrogen produced is the same as heat of combustion. Each hydrogen molecule is formed by the addition of two electrons to two hydrogen ions in solution, so that a direct relationship exists between the current passed (the electron flow rate) and the rate of hydrogen production (Faraday's law). Deviations from Faraday's law (which implies that 15.6 SCF* of hydrogen is produced per 1000 A-hr) are characterized by the electric-current efficiency of the cell. The current efficiency in most cells approaches 100%. Any lower efficiencies experienced are the result of extraneous electrode reactions during the electrolysis; but, theoretically, no alternative chemical reactions can occur except the recombination of hydrogen and oxygen in solution. A perfectly efficient cell would require 94 kWhr of electrical energy for each 1000 SCF of hydrogen produced. Of these 94 kWhr, only 79 need be supplied as electrical energy; the remainder can be supplied as heat. Because this energy input to the cell is in the form of power (the product of voltage and current), each electrolytic process has a theoretical voltage corresponding to the energy required for the reaction to proceed.

In electrolysis, only the free energy of reaction, ΔG, can be interchanged with electrical energy at constant temperature and pressure. The quantity of electric charge corresponding to the molar quantities indicated in the balanced chemical equation is nF, where n is the number of electrons transferred per molecule and F is the Faraday value. If this quantity of electrical charge is transported through a potential difference of E volts, the amount of work required is given by nFE. Because this electrical change does not involve pressure-volume work and is carried out isothermally, the change in Gibbs free energy is given by —

$$\Delta G = -nFE \qquad (3\text{-}1)$$

where E is the potential difference, or voltage, which by convention is taken as positive. If ΔG is negative for a spontaneous cell reaction and E is taken as positive for a spontaneously discharging cell, there results a negative sign in Equation 3-1.

The entropy change for an electrolytic-cell reaction may be calculated from the temperature coefficient of the electromotive force because —

* All cubic feet measurements given in this section are at standard conditions, 68°F and 14.7psi.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \Delta S$$

Introducing this into Equation 3-1, we have –

$$nF\left(\frac{\partial E}{\partial T}\right)_p = \Delta S \qquad (3\text{-}2)$$

The enthalpy change for the cell reaction may be calculated by substituting Equations 3-1 and 3-2 into –

$$\Delta H = \Delta G + T\Delta S = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p \qquad (3\text{-}3)$$

It is apparent from Equation 3-3 that the difference between the free-energy change and the total-energy change (enthalpy) is accounted for by an entropy change in the process. Because the entropy change cannot be converted to electricity, it must be supplied or liberated as heat.

For a water electrolysis cell, we can calculate that the voltage corresponding to the enthalpy change, or the heat of combustion of hydrogen, is 1.47 volts at 25° C (77° F), whereas the cell voltage corresponding to the free-energy change is only 1.23 volts.

In an ideal case, then, 1.47 volts applied to a water electrolysis cell at 25° C (77° F) would generate hydrogen and oxygen isothermally – that is, at 100% thermal efficiency with no waste heat produced. However, a voltage as low as 1.23 volts would still generate hydrogen and oxygen, but the cell would absorb heat from its surroundings. The electrical energy required for the process is only 83.7% of the combustion energy of the hydrogen produced; the other 16.3% is supplied as heat. Another way of expressing this is that the fuel value of the hydrogen produced is 120% of the heating value of the electrical energy input.

In practical cells, there is usually an efficiency loss that is greater than the difference between the free-energy voltage and the enthalpy voltage. In other words, practical cells usually operate at voltages greater than 1.47 volts and liberate heat because of a variety of efficiency losses occurring within the cell. The heat required to supply the entropy of reaction is therefore provided by some of this waste heat, and practical cells do not absorb heat from their surroundings. If an extremely well performing cell could be operated at a voltage below 1.47 volts, it would act as a refrigerator, drawing

heat from its surroundings to make up the deficit in the energy input. There seems to be little chance of developing electrolyzer cells that operate so close to the ideal that they do, in fact, act as refrigerators. However, there seems to be a reasonable chance of obtaining cell operation at 1.47 volts, which would represent an apparent 100% conversion of electrical energy to the fuel value of hydrogen. If such a cell performance can be achieved and an apparent cell efficiency of 100% is demonstrated, this would still represent an electrochemical efficiency of only 83%. It is curious, therefore, that a practical device could probably be produced that operates at an apparent efficiency of 100% without violating the basic laws of thermodynamics. This operating voltage of 1.47 volts is a good target to aim for in the development of advanced electrolyzer cells.

The free-energy-change voltage, E, or "reversible" voltage as it is called, varies with temperature as shown in Figure 3-1. As can be seen, raising the temperature lowers the voltage at which water can be decomposed. This factor operates in favor of electrolysis cells because at higher temperatures the electrode processes proceed faster, with less loss, while the required energy input is less. This is in contrast to fuel cells; their available energy output falls as the temperature is raised.

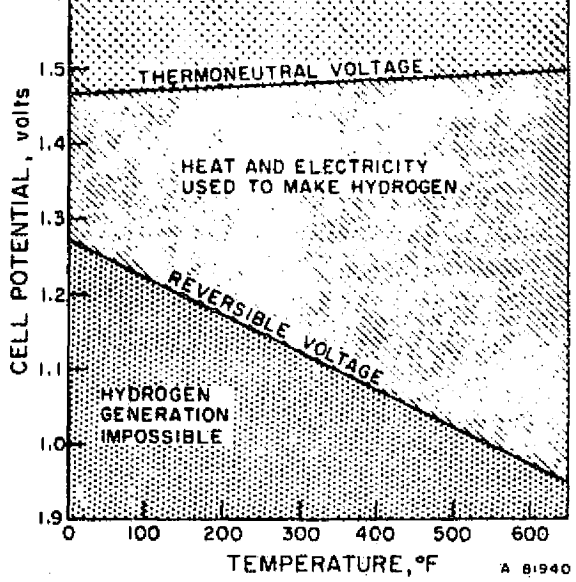


Figure 3-1. IDEALIZED OPERATING CONDITIONS FOR ELECTROLYZER[17]

The voltage corresponding to enthalpy change, or as we shall term it, the "thermoneutral voltage," varies only slightly with temperature, from 1.47 volts at 25° C (77° F) to 1.50 volts at 340° C (644° F). This is also shown in Figure 3-1. Three areas, therefore, can be identified: 1) that in which no hydrogen is evolved, 2) that in which hydrogen is made at an apparently greater-than-100% efficiency, and 3) that in which hydrogen is made at an efficiency of less than 100% with the production of waste heat.

Effect of Pressure on the Decomposition Voltage

In considering the theoretical aspects of the effect of pressure on electrolysis, we have to inquire into the effect of pressure on the decomposition voltage and on the efficiency losses within the cell. During electrolysis the free-energy change can be written as –

$$dG = -SdT + VdP \tag{3-4}$$

If we apply this at constant temperature we can write –

$$\frac{\partial Gp}{\partial P} - \frac{\partial Gr}{\partial P} = Vp - Vr \tag{3-5}$$

where G_r, G_p, V_r, and V_p are the Gibbs free energies and volumes of the reactants and products, respectively. This equation may be written –

$$\frac{\partial \Delta G}{\partial P} = \Delta V \tag{3-6}$$

where ΔV is the change in volume during reaction. Substituting ΔG into Equation 3-6 we obtain –

$$\frac{\partial E}{\partial P} = \frac{-\Delta V}{nF} \tag{3-7}$$

If we assume that the volume of the liquid water is small compared with that of gaseous products hydrogen (H_2) and oxygen (O_2), and if we further assume the volumes of these gases obey the perfect gas law –

$$PV = ZRT \tag{3-8}$$

where Z = number of moles, we derive –

$$dE = \left(\frac{ZRT}{nF} \quad \frac{dP}{P}\right)_{O_2} + \left(\frac{ZRT}{nF} \quad \frac{dP}{P}\right)_{H_2} \tag{3-9}$$

By integration between ambient conditions and the operating pressure we obtain –

$$E_p = E_1 + \frac{0.052}{2} \log P_{H_2} + \frac{0.058}{4} \log P_{O_2} \tag{3-10}$$

Because during electrolysis $P_{H_2} = P_{O_2}$ —

$$E_p = E_1 + 0.0435 \log P \qquad (P = \text{atm}) \qquad (3\text{-}11)$$

Thus, raising the pressure of operation of a water electrolyzer results in a theoretical increase in the decomposition voltage of 43 mV for every tenfold increase in pressure. The energy required to provide this additional voltage is exactly equal to the potential energy contained in the high-pressure hydrogen. In practice, electrolyzer cells operate slightly closer to the ideal at higher pressures than they do at atmospheric pressure — that is, efficiency losses are less at higher pressures. This is because of a variety of reasons, including the fact that the gas bubbles evolved are smaller and provide less hindrance to the passage of ionic current across the cell. At pressures of up to about 400 psia, the saving in energy due to increased efficiency is greater than the extra energy that has to be expended to overcome the theoretical voltage. Thus, pressurized operation of electrolyzers is an extremely efficient way of generating pressurized hydrogen; and, up to moderate pressure increases, pressure can be developed at "apparent" pumping efficiencies of greater than 100%.

In addition to the energy required to pass current through the electrolyzer cell itself, certain parasitic energy requirements must be met. Most practical electrolyzer systems contain pumps for circulation of the electrolyte, gas, or cooling fluid; and these consume small, but significant, quantities of energy. The power supplied to the cell must be relatively low voltage dc, although power supplies are conventionally high-voltage, 3-phase ac. The conversion of ac line power to dc power is not carried out with 100% efficiency; and the power-conditioning equipment, therefore, represents a further parasitic energy load on the system. These parasitic energy loads amount to somewhat less than 5% of the total energy consumption of an electrolyzer system.

Returning to the electrolyzer cell itself, the energy requirements of a practical cell are always greater than the minimum theoretical energy requirements described above. Efficiency losses occur because of a) the resistance of the electrolyte itself, b) changes in the voltage of the electrodes due to concentration polarization (changes in the concentration

of hydrogen ions, oxygen ions, or water in the vicinity of the electrodes), and c) voltage gradients set up at the electrode-electrolyte interface itself due to the slowness of the electrode reactions. Additionally, there are small losses in the electronic conduction of current through the metal parts of the cell.

Because a practical cell operates at a higher voltage than the theoretical value of 1.23 volts (at room temperature and pressure), the difference between the actual applied voltage and the theoretical voltage is commonly called overvoltage. The change in voltage at individual electrodes is often called polarization, and the terms overvoltage and polarization are used synonymously. The voltage efficiency of the cell can be determined by comparing the actual operating voltage with the theoretical voltage at the operating conditions. The operating voltage of a cell varies according to the current that is passed through it. Just as in an ohmic resistance, increasing the current results in an increase in voltage. Thus, the voltage efficiency of an electrolyzer cell is a function of the current passed through it, decreasing as the current is raised. If the operating voltage of the cell is plotted against the current per unit area of electrode, commonly termed the current density, a characteristic curve, commonly called a polarization curve, is obtained. This curve is a vital design parameter for an electrolyzer system because it shows the relationship between voltage for efficiency and the current density for the rate of hydrogen production. Clearly, by doubling the rate of current density, and thus doubling the hydrogen-production rate, the effective capital cost of the cell is halved, although efficiency is penalized. The polarization curve can be used to show a trade-off between capital cost and efficiency in determining an optimum operating point.

The current required to decompose water is determined simply by the fact that two electrons are needed to discharge one molecule of hydrogen. This corresponds to 15.6 SCF of hydrogen produced/1000 A-hr. In practical cells, high current efficiencies, approaching 100%, are usually achieved because there usually is no other path for the current to take. When multiple cells are connected together in series and use a common electrolyte, some current can short-circuit from one end of the cell stack to the other through the electrolyte feed channels. This only occurs with certain cell designs and results in a slight loss of current efficiency. Another source of efficiency

loss is the recombination of hydrogen and oxygen because they dissolve to some extent in the electrolyte and crossover into the separator. This loss becomes more pronounced when cells are operated at high pressures because of the increase in solubility. In practical low-pressure cells, current efficiencies in excess of 98% are usually obtained. The energy efficiency, or power efficiency, of a cell is therefore largely dependent upon the voltage losses or polarization of the cell, which remains the most important characteristic in determining the energy requirements for the practical electrolyzer cell.

Basic Designs of Electrolyzer Cells[4]

The oldest form of industrial electrolysis of water uses the tank electrolyzer in which a series of electrodes, anodes and cathodes alternately, are suspended vertically and parallel to one another in a tank partially filled with electrolyte. Alternate electrodes, usually cathodes, are surrounded by diaphragms that prevent the passage of gas from one electrode compartment to another. The diaphgram is impermeable to gas, but permeable to the cell's electrolyte. The whole assembly is hung from a series of gas collectors. A single tank-type cell usually contains a number of electrodes, and all electrodes of the same polarity are connected in parallel, electrically, as pictured in Figure 3-2. This arrangement allows an individual tank to operate across a 1.9 to 2.5 volt dc supply. In general, the cost of electrical conductors increases as the current load increases, but the cost of ac-dc rectification equipment per units of output decreases as the output voltage increases. This is one important consideration in the design of tank-type electrolyzers.

There are two major advantages to tank-type electrolyzers:

1. Relatively few parts are required to build a tank-type electrolyzer, and those parts that are needed are relatively inexpensive. Because of this feature, tank-type electrolyzers tend to optimize at a lower thermal efficiency than do more sophisticated electrolyzer structures. Therefore, tank-type electrolyzers are usually selected when electric-power costs are at their lowest.

2. Individual cells may be isolated for repair or replacement simply by short-circuiting the two adjacent cells with a bus bar. This feature allows maintenance to be carried out with a minimum of downtime for the entire plant.

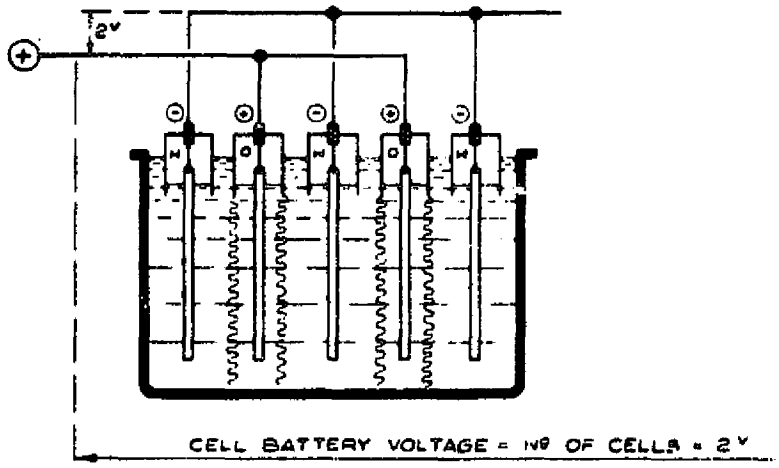


Figure 3-2. SCHEMATIC DIAGRAM OF A UNIPOLAR (Tank-Type) ELECTROLYZER [14]

The major disadvantages of tank-type electrolyzers are a) their inability to operate at high temperatures because of heat losses from the large surface areas; b) their requirements for more floor space than other types of electrolyzers (a point disputed by some proponents of tank-type electrolyzers, who state that tank cells can be accommodated in as small a floor space as the filter-press type), and c) the difficulty of designing the tanks to operate at high pressures.

As an alternative to tank-type electrolyzers, more recent electrolyzer designs use stacks so that the positive electrode of one cell is directly connected to the negative electrode of the next. An assembly of cells has superficial resemblance to a filter press because the electrolyte is manifolded to flow through each cell in parallel while hydrogen and oxygen exit lines are similarly manifolded through the stack.

Figure 3-3 is a schematic of a filter-press cell construction. This type of cell is sometimes called a bipolar cell (in contrast to the monopolar assembly in the tank-type cell) because each electrode is used with one face as the positive electrode of one cell and the opposite face as the negative electrode of the next cell. In practice, filter-press-type cells are usually constructed with separate electrodes in each cell that are electrically connected through a solid metal separator plate that serves to keep the hydrogen cavity of one cell separate from the oxygen cavity of the next. Because the cells of the

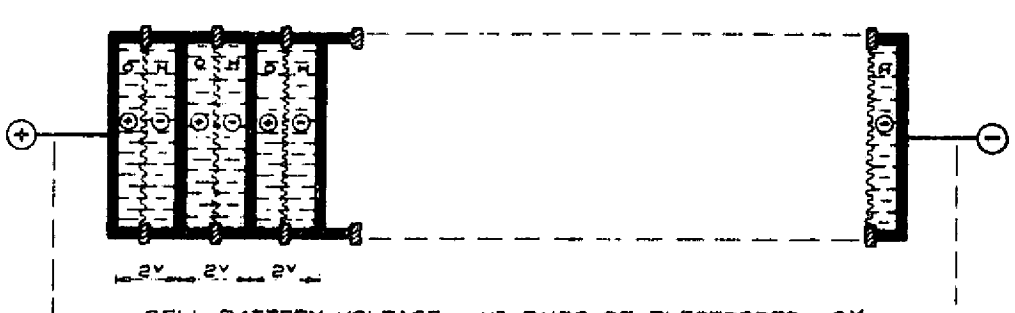


Figure 3-3. FILTER-PRESS (Bipolar) CELL CONSTRUCTION[13]

filter-press-type electrolyzer can be relatively thin, a large gas output can be achieved from a relatively small piece of equipment. It is usually necessary to cool the cells by circulating the electrolyte through them, and the electrolyte exiting from the cell carries with it the gas produced. In many designs, separation of the gas from the electrolyte is accomplished in a separating drum mounted on top of the electrolyzer. The electrolyte, free of gas, is recirculated through the cells. The major advantages of filter-press-type electrolyzers are that a) they take up less floor space than the tank-type design, b) they are more amenable to operation at high pressures, and c) they are more amenable to operation at high temperatures. The major disadvantages are that a) they require a much closer tolerance in construction because of sealing problems, and b) they are more difficult to maintain because if one cell fails, the entire battery has to be dismantled, and production of hydrogen is lost.

Filter-press electrolyzers usually present higher capital costs per unit area than tank-type cells; and, to compensate for this, they are operated at higher current densities.

Cells that use a solid-polymer electrolyte are usually constructed on the filter-press-type design. They do not require electrolyte circulation because the electrolyte is immobilized in the form of an ion-exchange resin. The electrodes are either embedded in the surface of the resin sheets or pressed closely against the two opposing faces of the sheet of resin material. A ribbed or corrugated solid-metal separator plate is interposed between cells, providing electric continuity between one cell and the next while separating the hydrogen from the oxygen in adjacent cells. This type of cell is usually

cooled by circulating water through the cavity between the metal separator and the electrode plate. Hydrogen or oxygen evolved into this cavity is swept out by the coolant stream and is separated from the water outside the cell. The advantages of the solid-polymer-type cell are that a) the electrolyte membrane or diaphragm can be made very thin, allowing high conductivity without risk of gas crossover, and b) the electrolyte is immobilized and cannot be leached out of the cell. The disadvantages of the solid-polymer-electrolyte (SPE) cell are that a) the electrolyte costs more than the conventional alkaline solutions and b) the electrolyte is corrosive and requires more expensive metal components to be used in the cell. For these reasons, solid-polymer-electrolyte cells are usually operated at somewhat higher current densities than cells that use a liquid alkaline electrolyte.

Electrolyzer-System Designs

A total electrolyzer system consists of all the equipment necessary for the process, from the input of electrical power to the output of hydrogen and oxygen gas at the appropriate purity and pressure levels. In addition to the electrolyzer cell module itself, which has already been described, three major subsidiary systems can be used in various forms.

Power Supply

For relatively large-scale electrolyzer systems, power is usually supplied from a three-phase, high-voltage line. To convert this into the relatively low voltage dc power needed for the electrolyzer cell, a combination transformer-rectifier unit is usually used. There is a trade-off to be to be made in the design of the transformer-rectifier system, which can provide dc at relatively high or relatively low voltages. By connecting the cells in series, high-voltage dc systems can be used, and this can have some cost advantages in the requirements for transformers and rectifiers. For reasonably large systems, dc voltages of 70 to 100 volts are usually used. Clearly, this is not possible with very small units because a large number of very small cells would be needed.

The cost of a transformer-rectifier system is considerable and can represent as much as 1/3 to 1/2 of the cost of the entire system. If electric power is being generated onsite, some consideration should be given to the direct generation of dc power and to the use of this for electrolysis. There seem to

be no examples of this in other electrochemical installations, for example, in chloride-caustic plants or aluminum-smelting installations that use onsite power. However, recent developments in the technology of acyclic or dc generators may make the direct reduction of dc power more promising. Modern, acyclic dc generators operate only at low voltages and this implies the use of very large currents, very large bus bars to distribute the power to the electrolyzer cells, and very complicated switch gear for handling high-current, low-voltage dc. On the other hand, dc generators apparently can be produced for about the same cost as ac generators; and the use of the dc system could considerably reduce capital costs that would otherwise be required in the provision of transformer-rectifier units. At present, not enough information is available to draw any conclusions about the relative merits and disadvantages of the ac versus dc supply systems.

Cooling Systems

Because electrolyzer cells are not, in fact, 100% efficient, a considerable amount of waste heat is generated in the electrolyzers and must be removed from the cells. There are several ways of doing this: a) by circulating electrolyte, b) by circulating hydrogen, c) by circulating water through the cell, and d) by circulating water through a heat exchanger in contact with the cell.

Circulation of electrolyte requires a pump capable of handling a corrosive liquid at relatively high temperatures and possibly at a high pressure. If electrolyte is circulated through a common manifold through a large number of cells connected in series, then a high voltage is applied to it from one end of the manifold to the other. This induces a short circuit through the electrolyte, thus utilizing only the electrodes at either end of the cell stack. There is a trade-off between the reduction of this short-circuit current or "shunt current," which results in low current efficiency of the entire cell stack, and the deliberate introduction of high-resistance paths in the electrolyte circulation loop, which result in a requirement for high circulating pumping power. In some types of cells, notably the tank-type cells in which the electrolyte in each cell is kept entirely separate from that in all others, these shunt currents are not possible. The circulation of electrolyte in these cells is usually provided by the gas-lift effect of the gases being evolved at the electrodes. Thus, very little parasitic energy is required, and no electrolyte

circulating pump is needed. However, the circulation rates achieved by this means are not usually sufficient to remove the generated heat from the cell, but simply serve to stir up the electrolyte to reduce concentration gradients resulting from the removal and replacement of water.

Hydrogen itself can be used as a heat transfer material by circulating it repeatedly through the cell. Again, a circulating pump is required that can handle hydrogen, sometimes in the presence of traces of electrolyte. Hydrogen is withdrawn from the circulating loop at the rate at which it is produced at the electrode, and the circulating loop contains the heat exchanger by which the waste heat of the cell is removed.

In the SPE-type cell, it is possible to circulate water through the cell, in contact with the electrolye, without leaching out the electrolyte itself. This approach is not possible in a cell that uses an aqueous electrolyte solution; and, in this case, a separate water compartment must be used. This is easier to achieve in a tank-type cell than in a filter-press type, although water-cooled plates can be built into stack-type cells. In some tank cells, a water chest, to act as a heat-removing mechanism, is incorporated into the design of the tank itself.

One of the problems of operating electrolyzer cells at very high pressures is that the auxiliary equipment, including the cooling system, would also have to be operated at high pressures; and thus the cost of even electrolyte and feedwater pumps, which in an atmospheric system would be insignificant, can become considerable.

Gas-Removal Systems

Once gas has been generated at the electrodes, it must be removed from the electrolyzer cell and conditioned to the temperatures, pressures, and purity levels required by the customer. There are two ways of removing the gas from the cell: One is to allow it to be entrained in the flowing stream of electrolyte, bring both out from the cell together, and pass the stream through an external separator. This usually makes the design of the electrolyzer cell itself more simple, but requires extra equipment for the separation of electrolyte from the gas. Clearly, two separator systems would be required – one for hydrogen and one for oxygen. The second method is to allow the gas to separate itself from the electrolyte within the cell and then remove it as a

gas stream only. In this case, it is likely to carry over a spray of electrolyte, and a spray trap of some sort is needed. Once hydrogen and oxygen have been removed from the cell, they must be dried because they are produced from the cell saturated with water vapor. After drying, they must be compressed if the cell is not operating at the required delivery pressure. This need for an external compressor increases the parasitic load or energy requirement of the overall cell system. The removal of small traces of oxygen from the hydrogen stream can be accomplished by use of a so-called "deoxo" catalyst. This catalyst is usually a high-surface-area palladium catalyst, supported on asbestos, that has the effect of causing the traces of oxygen to combine with hydrogen to form water. Because oxygen and water vapor are the only major impurities likely to be found in electrolytic hydrogen, drying and oxygen removal are the only purification steps necessary for obtaining very high purity hydrogen.

Survey of Types of Industrial Electrolyzers

The Electrolyser Corporation

The Electrolyser Corporation Ltd., of Toronto, Canada, produces tank-type electrolyzers that use potassium hydroxide as the electrolyte. Their cell designs are known as Stuart cells and are sold in many parts of the world. A Stuart cell consists of a nickel-plated steel cell tank with positive and negative electrodes arranged alternatively and suspended from the cell cover. Electrodes in a single-cell tank are connected in parallel, and the cell tanks are connected in series to form a cell battery and to promote a higher overall voltage, consequently lowering rectification costs. This arrangement results in an operating voltage of approximately 2 volts dc, even in large cells.

Electrodes used in these cells are made of high-conductivity, high-surface-area, sand-blasted steel; the anodes are nickel plated to prevent corrosion. As in most tank electrolyzers, each anode is surrounded by a woven asbestos cloth diaphragm that prevents the mixing of hydrogen and oxygen. It also channels the oxygen generated toward a storage chamber beneath the cell cover. Hydrogen formed at the cathodes rises between the diaphragm to the hydrogen compartment under the cover. It is not uncommon for these diaphragms to last well over 20 years without replacement.

According to A. K. Stuart, the unique and proprietary construction of the Stuart-cell electrodes provides a large surface for electrolysis in a mini-

mum of space. Because of the large active surfaces of the electrodes, Stuart says the cells are able to operate at a high total current with the surfaces exhibiting low current densities. Details of electrode construction are not publicly available.

The low cell-operating voltage and the physical separation of each cell tank simplifies electrical insulation within each cell and enables efficient sealing against loss of the electrolyte and gas product. The electrolyte is circulated independently within the cell by means of the lifting effect of the rising gas bubbles. This method requires no moving parts and avoids the hazards and complexity associated with external electrolyte pumping systems. A 10 to 15 year or more life span is customary before the electrolyte needs to be replaced. A 28% potassium hydroxide solution is the recommended electrolyte for the Stuart cell.

Each of the Stuart cells is automatically supplied with feedwater through individual valves set to maintain correct electrolye levels and concentrations. A cooling-water header passes along the rear of the cell tank, supplying individual hydrogen and oxygen scrubbers at the cell's gas outlets and a cooling jacket on the back of each cell. The water flow is adjusted to maintain optimum cell temperature; the effluent water is suitable for recycling. As is common with many tank electrolyzers, the Stuart cell operates at a rather low temperature, 158° F (70° C), and low current density, which minimizes waste-heat production. Under these conditions, overall cell efficiency is higher at all levels of hydrogen output than it would be if the cell were operated at high current densities.

The Stuart cell is rugged and simple to assemble and maintain, and the component parts are inexpensively fabricated. Hydrogen is produced at a 99.9% purity. Because the Stuart cell is contained in a closed system (not exposed to the atmosphere), the problem of formation of potassium carbonate from combination with the carbon dioxide in the air is not experienced.

The basic Stuart hydrogen plant is of modular construction in that an unlimited number of cells may be connected in series. Thus, hydrogen production capacity may be increased by simply adding more cells.[14] Plants consist of assemblies of cells, each 44 inches long and 49 inches high, ranging in width from 12 to 33 inches according to the number of electrodes and output capacity. Standard cells produce from 63.6 to 350 CF of hydrogen per hour

and weigh from 1665 to 5135 pounds. Standard production rates for these cells, per 1000 amperes of current, are 15.9 CF of hydrogen per hour and 7.95 CF of oxygen per hour. The dc power consumption is 128 kWhr/1000 CF of hydrogen. Maximum gas production pressure is slightly above atmospheric (10 inches, water column).

Typical Stuart hydrogen plants produce hydrogen at the rate of tens of thousands of cubic feet per hour. The utility requirements of a typical Stuart electrolyzer plant are as follows: For 1000 CF of hydrogen and 500 CF of oxygen, electric power consumption (ac) is 133 to 145 kWhr; the demineralized feedwater required is 0.895 CF; and the cell cooling water required is 38.77 CF.

Some uses for hydrogen outputs in the tens of thousands of cubic feet per hour include the manufacture of semiconductor materials; that of hydrogen coolant at thermal and nuclear power stations; the synthesis of chemical intermediates for long-chain polymer production; the hydrogenation of oils and fats in margarine, shortening, and soap production; the direct reduction of metal oxides; the annealing of stainless and electrical steels; and that in float-glass manufacture.

Electrolyser Corporation makes a smaller unit known as the Stuart Packaged Hydrogen Generator. The generator is a self-contained, factory-assembled unit capable of producing pure hydrogen in quantities of from 20 to 1000 CF/hr.

Some applications for these smaller units include hydrogen for laboratories, the inflation of meteorological balloons, hydrogen and oxygen for cutting and welding, and the sintering of metal powders.

According to Stuart, both cell improvements and total hydrogen plant development are necessary to improve Stuart-cell hydrogen production. An increase in cell operating temperatures (a 2-year goal), from the current 158° to 194°F, is expected to increase the overall thermal efficiency by lowering the operating voltage. Stuart's 2 to 3 year goals for electrolyzer development include an electric-power consumption of 22.9 to 24.6 kWhr/lb of hydrogen produced, an operating voltage of 1.9 to 2.04 volts, and a thermal efficiency of 77%.

Stuart feels that some exploration of advanced diaphragm materials, to handle the higher temperatures of operation, will be necessary. Present

asbestos diaphragms can possibly handle these temperatures, but the upper limits consistent with a satisfactory life span are not yet known. Life testing is now being performed. Continued development of electrodes has the potential of lowering cell overvoltage.

Some scale-up of present cells is expected; however, overall plant development is necessary to provide the best economics. The economic conversion of shaft power to high dc current is considered by Stuart to provide the best opportunity for improved operation of his cells. Acyclic generators rated at 250,000 amperes (dc) would be connected directly to high-current cells. Acyclic generators would not require the switchgear or transformers needed with the more conventional ac-dc rectification equipment. The capital costs for conventional ac-dc conversion are approximately $40/kW, whereas capital costs for an acyclic generator are expected to be about $10/kW.

According to Stuart, no heat-transfer problem is expected when his cells operate from a 250,000-ampere dc source. Heat transfer associated with Stuart-cell scale-up has not posed any problem in a series of scale-ups. Stuart cells operate at a current density of 125 A/sq ft and have gone up to 500 A/sq ft without evident heat difficulty.[13]

Teledyne Isotopes, Inc.[4,5,16]

Teledyne Isotopes, of Baltimore, Md., acquired the fuel-cell and electrolyzer R&D technology that had been developed by Allis-Chalmers Corp. up until 1967. Teledyne manufactures, or can build to suit a user's requirements, three families of hydrogen producing electrolyzers: 1) generators that produce from 0.177 to 0.353 CF/min, 2) systems that produce from 0.177 to 7.06 CF/min, and 3) plants that produce several tons/day.[4] Plants in categories 1 and 2 have been sold commercially, but plants in category 3 have yet to be ordered and built.

The current Teledyne Electra cell systems are of filter-press type and, in general, consist of modules made of multiple electrolysis cells connected in series, electrically, by common bipolar plates. The electrodes are separated by a matrix saturated with electrolyte. The matrix prevents mixing of the gases and provides a conductive path for the electrode current. As the hydrogen and oxygen are formed, they are kept apart; and the gases from each cell are ducted internally, through manifolds, to storage containers.

The electrolyzer uses a potassium hydroxide-water solution (25% by weight) electrolyte with advanced-design, porous nickel electrodes and operates at moderate temperatures, 100° to 200°F. The cell contains no precious-metal catalysts.

Various subsystems support the electrolysis module by recirculating and cooling the electrolyte, adding water, conditioning the product gases, and supplying electricity.

Small hydrogen generators that produce from 0.177 to 0.353 CF of hydrogen/min are used for such applications as producing carrier gases for gas chromatographs and fuel for flame-ionization instruments, primarily in the pollution-control and monitoring industry. These small generator units operate from a standard 110 volt (ac) power source and delivery hydrogen at from 0 to 35 psig with a purity of better than 99.99%.

A schematic diagram of the generator system is provided in Figure 3-4. The electrolyte is recirculated on the oxygen side of the module to supply each cell with water and to remove heat. The generation of oxygen gas in the cell provides a gas-lift effect for convective circulation, thereby eliminating the need for a pump. While auxiliaries are available to provide for con-

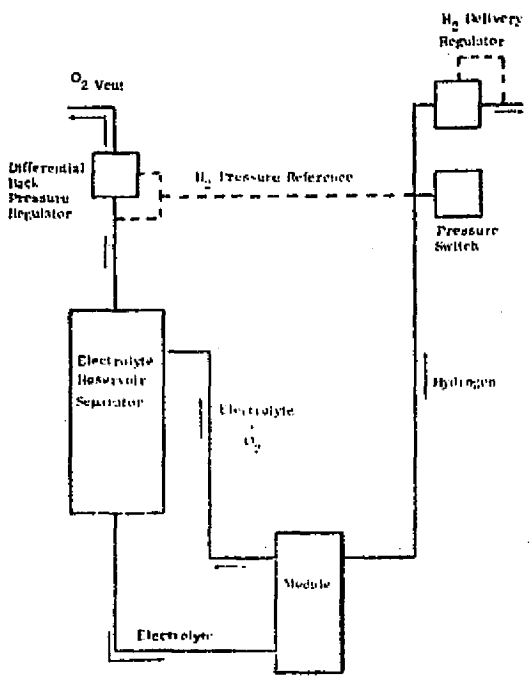


Figure 3-4. SMALLEST TELEDYNE HYDROGEN GENERATOR[7]

tinuous water replacement, the basic system operates on a batch-feedwater refill technique. In most cases, heat is removed at the electrolyte reservoir by natural convection to the ambient air, allowing the system to operate at less than 130°F.

Larger quantities of hydrogen are produced with the Teledyne intermediate-size electrolysis systems. Where larger quantities of hydrogen are needed for industrial processing, such as in the production and sintering of metal powders of iron, nickel, cobalt, and molybdenum, for the bright annealing of stainless steels, or in electrical-utility use, Teledyne electrolysis units have been sized to provide from 0.177 to 7.06 CF of hydrogen/min. Increased capacity and optimum equipment utilization can be provided by using multiple units.

This system differs from the smaller generator in that the electrolyte is recirculated on the oxygen side of the module by a centrifugal pump. This arrangement resupplies each cell with water, removes heat, and carries away generated oxygen. A tube-and-shell type heat exchanger is provided to transfer heat to a water cooling loop. Usual system operating temperatures are less than 185°F. Oxygen is separated from the electrolyte in the electrolyte reservoir, where the supply of water is also renewed. The separated oxygen flows through a condenser to remove excess moisture and then flows to a pressure-control device to regulate and control the oxygen and electrolyte loop pressure. Hydrogen generated in the module is manifolded and is piped directly to a condenser for removal of most of the water vapor and then to a molecular sieve dryer.

These larger systems weigh from 1000 to 2000 pounds per cabinet and have dimensions of 33 x 74 x 64 inches. Facilities to supply 460-volt (ac), three-phase electricity, cooling water, feedwater, and a small amount of inert gas are the only other facilities required. This system requires a minimum of maintenance. The electrolyte is sampled once a month to determine its specific gravity. After the initial electrolyte change at the end of the first month of operation, the electrolyte is changed only semiannually. Semiannual changing of the electrolyte filter, water-flushing of the solenoid valves, and calibration of the pressure switches are recommended.

When quite large quantities, several tons per day, of hydrogen are required, Teledyne recommends a considerably different system of hydrogen production. A schematic diagram of this system is shown in Figure 3-5. In this system, the electrolyte circulates to both sides of the electrolysis module, which allows for more efficient heat removal and simplifies the pressure-control function. The electrolyte is recirculated by a single pump to both the hydrogen and oxygen cavities of the module. Each gas and electrolyte mixture is then returned to a different reservoir and separator where the gas and liquid phases are separated. The electrolyte is cooled in a heat exchanger and then mixed with electrolyte from the opposite portion of the system. Replacement water is continuously added at the mixing chamber. The gases are piped through condensers to remove excess moisture and then through a pressure-control device and are finally delivered for use. With this system of "double flooding" the gas-collection chambers, there is a) no pressure differential across the diaphragm or pushing away of the electrodes, which may occur with a large enough pressure differential, b) no concentration gradient across the cell, and c) a more economical production of hydrogen because more hydrogen is

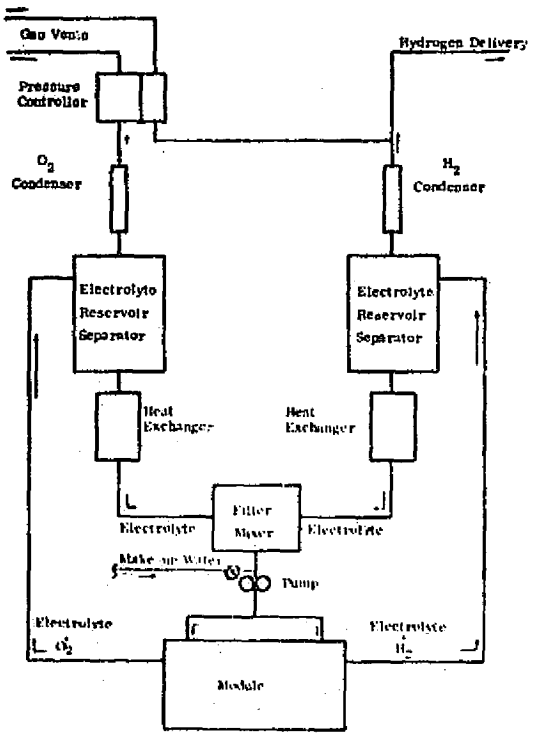


Figure 3-5. LARGER-MODEL TELEDYNE HYDROGEN GENERATOR[7]

being produced while the costs and requirements of auxiliary equipment remain the same. Simple pressure-control devices are incorporated in this cell system to allow an operation of up to approximately 100 psig.

These systems can be controlled to provide constant gas-production rates and a specified level of gas purity. Multiple-system packages can be installed to supply virtually an unlimited quantity of hydrogen. Each system occupies approximately 260 cu ft of floor space and will generate hydrogen at an efficiency of 140 kWhr/1000 SCF.

Although none have been built, Mr. W. C. Kincaide of Teledyne states that the hydrogen plants producing 1 to 4 tons of hydrogen/day would operate at an electrical-conditioning efficiency of 95% and at an electrolysis efficiency of 82%.

Future expectations for 2 to 5-year developments include electrolyzer cells consuming 19-22 kWhr/lb at an operating voltage of between 1.6 and 1.8 volts and an overall thermal efficiency of between 82 and 92%. Ultimate goals project the development of a cell that consumes 15 kWhr/lb of hydrogen and has an operating voltage of 1.24 volts at a 118% thermal efficiency, which is almost congruous with the thermodynamic limit.

Teledyne mentions certain goals yet to be attained. Increased operating efficiencies can be achieved by the use of noble-metal catalysts on the electrodes in the modules; but, in some cases, the additional increase in capital costs can more than offset any advantage gained. Teledyne is currently engaged in continuing the development of low-cost catalysts that would lower overvoltages.

Teledyne states that improvements in cell operating-temperature capability are expected within the next 2 years and should produce operating-efficiency improvements of 15%. Improvements in cell materials must also be developed to withstand the increased temperatures. It is expected that present asbestos diaphragms or gas separators will not be able to withstand increased temperatures of operation, and research is being undertaken to alleviate this problem.

Teledyne revealed that it has had problems in obtaining good commercially manufactured parts for its electrolyzers. In many instances it has developed its own system parts to meet close tolerances and specifications.

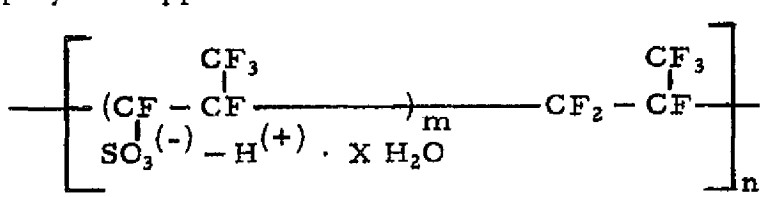
All Teledyne systems currently operate at pressures higher than ambient. An insignificant power penalty (0.431 kWhr/lb of hydrogen at 100 psia) is realized when compared with conventional compressors. Teledyne realizes the importance of the generation of hydrogen at high pressure to storing and transmitting large amounts of the gas. The operating pressures of present systems are limited by structural features. One specific question being reviewed by Teledyne is whether to design a cell stack to withstand pressure or to place a pressurized tank around an existing stack. Studies are being performed to determine the demand and cost effectiveness of high-pressure systems in commercial applications. Teledyne is building, for the U.S. Navy, electrolytic gas generators that operate at pressures of up to 3000 psig. Power penalties for generating gas directly at this pressure are less than 1.197 kWhr/lb.

General Electric Company [2, 11, 18, 19, 20]

General Electric Co. of Lynn, Mass., has been developing a water-electrolysis system based on solid-polymer-electrolyte (SPE) fuel cell technology. SPE fuel cells were first used in space during the Gemini Program, in which they provided primary on-board power for seven of the spacecraft flights.

According to staff at GE certain technological advances in the design of the SPE have resulted in a water-electrolysis unit of considerable simplicity in design and operation that can maintain stable and efficient use of relatively expensive electricity supplies.

The SPE is a thin, solid, plastic sheet of perfluorinated sulfonic acid polymer, which has many of the physical characteristics of Teflon. Chemically, the polymer approximates [20] —



Unlike Teflon, however, when a thin sheet of this material is saturated with water, the polymer becomes an excellent ionic conductor, providing low electrical resistance. Used in an electrolysis cell, it is the only electrolyte required; there are no free acids or alkalis in the system. Ionic conductivity

is provided by the mobility of the hydrated hydrogen ions ($H^+ XH_2O$), which move through the sheet of electrolyte by passing from one sulfonic acid group to another. Because the system is solid, the sulfonic acid groups are fixed, keeping the acid concentration within the electrolyte constant.

An important feature of the SPE system is the simplicity of the electrodes. Because the electrolyte is a solid, the catalytic electrodes are not required either to retain or support the electrolyte, and can therefore be optimized for catalytic activity at minimum cost. Currently, a thin layer of high-catalytic-activity platinum black is attached to the SPE surface to form the hydrogen electrode. A similar layer of a proprietary precious-metal-alloy catalyst forms the oxygen electrode. Additional metal current collectors are pressed against the catalytic layers. To date, the system has incorporated the use of niobium or titanium as the current-collector and separator-sheet material. Figure 3-6 is a schematic diagram of the SPE electrolysis cell.

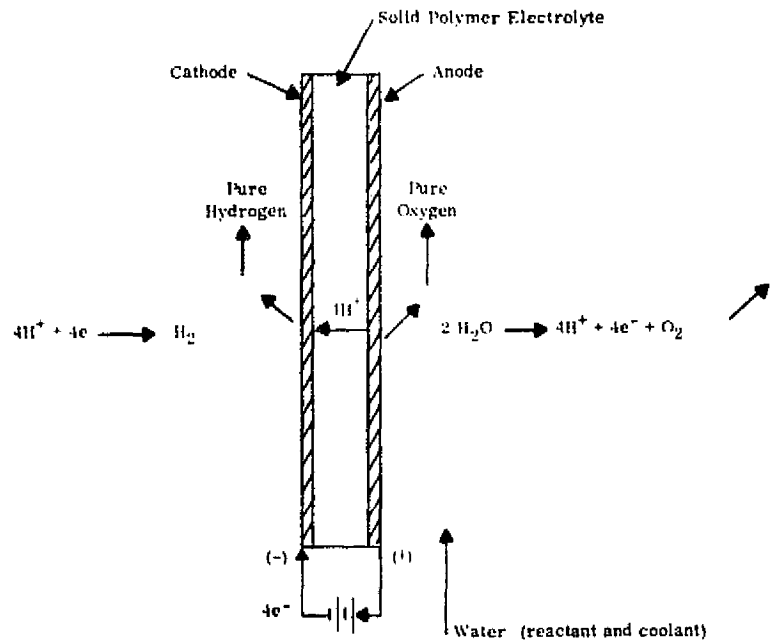


Figure 3-6. SCHEMATIC DIAGRAM OF AN SPE ELECTROLYSIS CELL[11]

In this configuration, water is supplied to the oxygen-evolving electrode (the anode), where it is electrochemically decomposed to provide oxygen, hydrogen ions, and electrons. The hydrogen ions move to the hydrogen-evolving electrode (the cathode) by migrating through the SPE. The electrons pass

through the external circuit and to the hydrogen electrode. At the hydrogen electrode, the hydrogen ions and electrons recombine electrochemically and produce hydrogen gas. An excess of water is usually supplied to the system and is recirculated to remove any waste heat.

The gases produced by the SPE are generated, at any pressure, in the stoichiometric ratio of hydrogen to oxygen. The electrolyte sheet can withstand pressure differences of up to 1000 psi, as well as high generating pressures (up to 3000 psi), simply by back-pressuring the system. The high generating pressures may be useful in solving transmission and storage problems.

According to staff at GE, use of the SPE results in the following advantages[18, 20]:

- The cell can operate with high differential pressures (>1000 psia) in addition to high gas-generating pressures.
- The concentration of the electrolyte is fixed, and the electrolyte is not mobile.
- There is no possibility of acid carry-over into the effluent gas.
- There are no corrosive electrolytes to control or that can leak in the system.
- The electrolyte is essentially invariant in operation.
- The acid-SPE electrolysis unit results in a minimum power requirement per unit of gas generated.
- High-current-density capability can result in an optimum design for low capital cost, as well as for low operating cost.

Although most of the SPE development was done for the space program and for aircraft applications, GE now produces two smaller hydrogen generators for commercial applications. Applications for these generators include the production of hydrogen for gas chromatographs and for flame-ionization detectors. At present, 22 kWhr of power are absorbed per pound of hydrogen produced at an operating voltage of 2.00 volts and a thermal efficiency of 74%.

The future of the GE cell seems to lie in operations at very high efficiencies, thus minimizing power costs and justifying the relatively high capital costs. Because these cells will also operate at higher current densities, a greater hydrogen-production rate per unit cost will be achieved. GE's objectives are to further improve the thermal efficiency of the SPE-cell system

and to develop lower cost materials and manufacturing processes to achieve an overall cost for large-scale electrolytic hydrogen production of $2 to $3/million Btu (based on 1974 costs), assuming electrical-power costs in the range of 5 to 10 mills/kWhr.

W. A. Titterington lists four specific elements to be included in a long-range development program: 1) electrolysis-module development, 2) system definition, 3) demonstration of a 5-MW prototype, and 4) incorporation of advanced technology.

SPE electrolysis-module technology is limited mainly by the cell operating temperature and by the lack of suitable cell-component materials. The importance of cell operating temperature is reflected by the fact than an increase in temperature from 80° to 220°F decreases power consumption by 10% with the same amount of hydrogen produced. At 300°F, if cell operating temperatures as high as this can be attained, the theoretical decomposition voltage of water decreases from 1.18 volts (at 180°F) to 1.12 volts. However, at 300°F the cell-sealing techniques or gasket materials may be a problem because they cannot withstand high temperatures and wet environments.

Experience has also been obtained at hydrogen gas generation pressures of up to 3000 psia. The resulting effect on performance is shown in Figure 3-7.

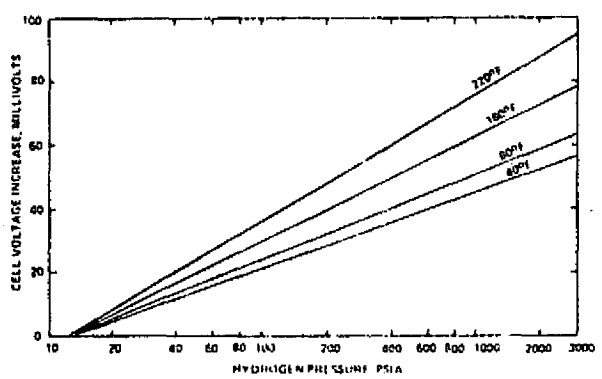


Figure 3-7. EFFECT OF HYDROGEN PRESSURE ON GE-CELL VOLTAGE[20]

To date, the SPE electrolysis systems have used niobium or titanium as the collector and separator-sheet material, in spite of statements that the SPE is noncorrosive. Niobium is quite expensive, $40 to $50/lb; titanium, however, has a more desirable price, $8/lb. GE states that alternative materials, including molybdenum, zirconium, and various alloys of these materials, should be tested for compatibility in high-temperature SPE electrolysis cells.

The SPE in the currrently manufactured cells is 12 mils thick. Considerable voltage reductions could be attained by halving this thickness. Representatives from GE have suggested that minor modifications in both the cell-fabrication technique and the hardware design would then be required. Further reduction in the thickness of the SPE could further lower the electrical resistances; therefore, more experiments are to be conducted along this line. It must also be remembered that as the SPE's thickness is decreased, its cost is also decreased. Alternative, lower cost SPE's (at as low as $2/sq ft) are currently under development.

Two other areas of research that may provide economic advantages for the SPE cell are decreases in the catalyst loadings on the electrodes and advancement of the catalytic electrodes. Progress in these areas could result in lower capital costs for the entire cell and in lower overvoltages at both the anode and the cathode. The present cathode catalyst is platinum black, with loadings of 4 mg/sq cm. A proprietary metal-alloy catalyst is applied to the anode, also at a loading of 4 mg/sq cm. Expectations of catalyst loadings as low as 1 mg/sq cm on each electrode are not unreasonable.

Life Systems, Inc.[3,12]

The static feedwater electrolysis system developed by Life Systems, Inc., under NASA sponsorship, has potential applicability for terrestrial hydrogen production. Developed for the space program, the static water electrolysis system uses a) an alkaline electrolyte; b) a method whereby the electrolyte is retained in a thin, porous matrix, eliminating bulk electrolyte; and c) a static water feed mechanism (depending on distillation of water inside the cell) to prevent electrode and electrolyte contamination and to eliminate the need for very pure feedwater.

In the static water feed system, the water to be electrolyzed is supplied to the cell electrolyte as a vapor. Each cell is divided into three main compartments: a water-feed compartment, a hydrogen-gas compartment, and an oxygen-gas compartment. Compartment separation and liquid-vapor phase separation are achieved by the capillary action provided by liquid-filled asbestos sheets. Catalyzed porous-nickel plaques support the cell matrix, forming a composite electrolysis site. Plastic screens similarly support the water feed matrix. The cell configuration is given in schematic form in Figure 3-8, and Figure 3-9 shows the principle of cell operation. The latter figure represents a thermally insulated box enclosing two bowls of electrolyte. When power is applied to the electrodes, water in the cell electrolyte is consumed. As a result, the concentration of the cell electrolyte increases, causing its vapor pressure to drop below that of the feed-compartment electrolyte. This difference in vapor pressure is the driving force that causes the water vapor to diffuse across the hydrogen cavity to the cell matrix.

Two major advantages to this cell system are apparent: 1) the product gases need not be separated from the feedwater or electrolyte, and 2) semipure water may be used because contaminants rarely lower the vapor pressure of the feedwater. The electrodes and electrolyte remain uncontaminated because the water comes to the hydrogen electrode as pure vapor. The only factor limiting impurities is the eventual blockage of the feedwater-matrix pores. The amount of water transferred is direrctly proportional to the difference in water vapor pressures of the cell and feed electrolyte.

The cell design utilized in the static feed system includes a bipolar-plate, filter-press ccnstruction with welded bus bars providing intercell current connection. The hydrogen electrode is placed directly on the cathodic current collector. Current then flows from the cathode, through the matrix, and to the oxygen electrode. An expanded nickel screen is placed on the back of the anode, providing both a path for the current and a space for oxygen evolution. A major portion of the cell's inefficiency in the electrolysis of water occurs at the anode, and this inefficiency results in waste heat that must be removed. The cell coolant passages were placed directly over the bipolar plate opposite the oxygen cavity. If air cooling is desired, this plate is extended out past the cell frame, forming external fins for convection or forced air cooling.[3]

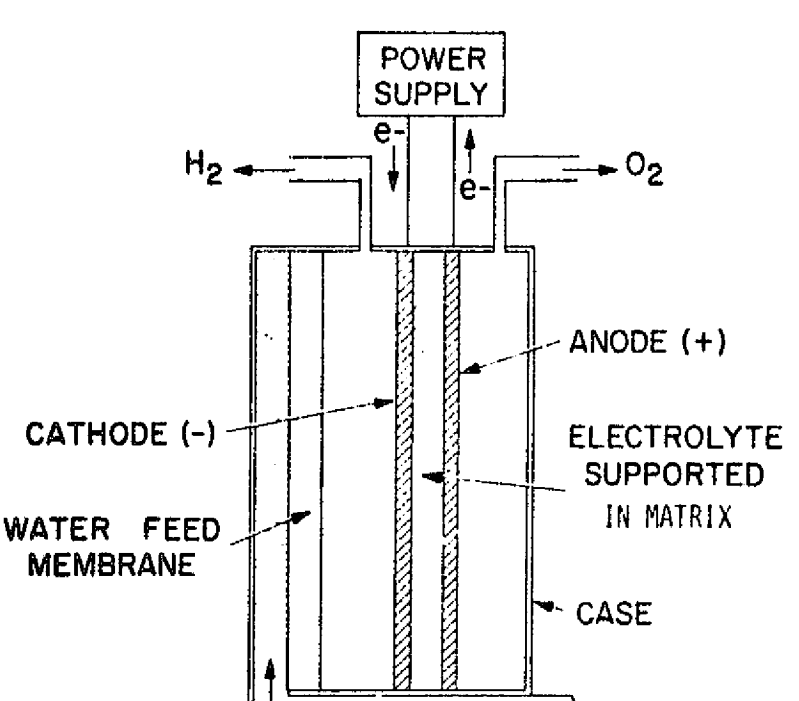


Figure 3-8. LIFE SYSTEMS CELL CONFIGURATION[3]

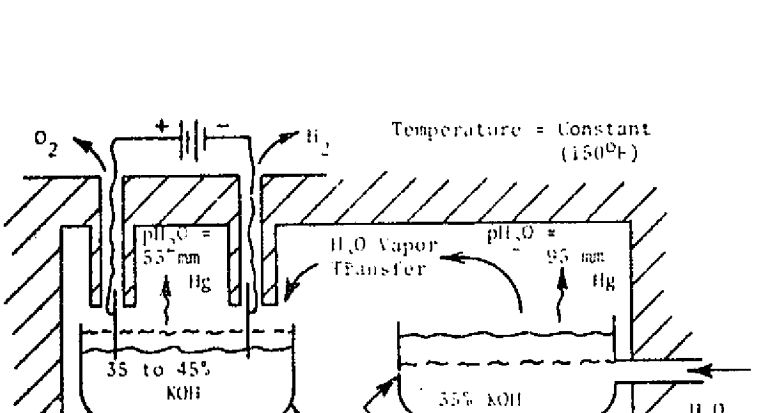


Figure 3-9. LIFE SYSTEMS CELL OPERATION[3]

Because Life System's electrolysis designs were developed for the space program, expensive materials were utilized to provide reliability and efficiency. The system cell frames are injection-molded from flame-resistant plastic. All metallic parts are made from nickel alloy, which is then gold-plated. Both the feedwater matrix and the cell matrix are made of Life System's reconstituted asbestos. Other cell materials include stainless-steel end plates and polypropylene screens used to provide structural support for the matrices.

The electrolyte used is a 35% potassium hydroxide-water solution instead of the more electrically conductive 25% to 28% solution.[3] At higher electrolyte concentrations and at higher temperatures, differences in the concentrations of the water feed and all the cell-matrix electrolyte result in greater water vapor partial-pressure differences. Because this difference is the driving force for the amount of water transferred, this phenomenon is accelerated.

The projected 1975 capabilities for Life Systems' s cells are –

- Maximum pressure, 2000 psi
- Maximum temperature, 300 ^{o}F (for short periods)
- Maximum current density, 1500 A/sq ft
- Power requirement, 129 kWhr/1000 SCF of hydrogen at 1500 A/sq ft
- Single-cell area, 0.10 sq ft.

At Life Systems, studies are under way on an alternative diaphragm material suitable for high-temperature (>200^{o}F) electrolysis. Potassium titanate has shown some excellent high-temperature and long-life stability capabilities. Additional studies are also being conducted on the availability of alternative structural materials suitable for high-temperature applications and enabling cell operation with lower electrolysis power requirements. Advanced designs, using zirconia and yttria-thoria ceramics for solid electrolytes, are being evaluated. These electrolytes conduct only at temperatures above about 1490^{o}F. Advanced catalyst development is also being performed to increase electrode performance and to lower costs. This work is being conducted in parallel with the high-temperature research in order to develop high-pressure, large-scale hydrogen generation.[3]

Lurgi GmbH [8,22]

Of the many electrolyzers produced in other countries, the Zdansky-Lonza electrolyzers, manufactured by Lurgi GmbH, Germany, are particularly noteworthy because these electrolyzers, working under a pressure of 30 atmospheres, are very economical, compact, and reliable. The Lurgi electrolyzer is basically of the filter-press type.

In each cell of the electrolyzer, between two round, nickel-plated discs pressed in nickel-plated gaskets, are pressed-metal screen electrodes, pressed-asbestos diaphragms, and sealing and insulating gaskets. The gas manifolds are located within the cells and are formed of Teflon rings: The holes in these provide passages from the inner space of the cells to the gas channels. The cells are very narrow, making it possible to connect several hundred cells (up to 500 cells in the largest electrolyzer) in one single apparatus.

Forced electrolyte circulation is used in the Lurgi electrolyzer. A pump forces cool electrolyte through an asbestos filter and into the lower manifold of the cell bundle. The electrolyte is cooled in the gas separators by means of coils built into storage drums through which the coolant and condensate circulate. The condensate is pumped through a closed loop and is cooled in an adiabatic heat exchanger. The total volume of condensate in the cooling system of an electrolyzer consisting of 250 cells with a capacity of 10,543 CF/hr of hydrogen is 28.25 CF.

Hydrogen and oxygen are manifolded into separate collection chambers. A floating valve is installed in the oxygen gas separator to regulate the escape of oxygen and to maintain a constant electrolyte level in the gas separator. Desalinated feedwater is provided to the cells by means of a variable-ratio pump, the capacity of which is adjusted manually, depending on the electrolyzer load.

If the level of the electrolyte in any of the gas-separator drums drops, the corresponding safety floating valve is opened; and the gas, the pressure of which was too high, is vented into the atmosphere. If the electrolyte level in one of the gas separators continues to drop, a magnetic relay shuts the electrolyzer down.

Lurgi produces only one size of electrolyzer, circular in shape and about 5 feet in diameter. Electrolyzer cells are assembled, at the factory, in blocks

of from 70 to 139 cells. These preassembled cell blocks can be installed at the operation site. Each block is pressed together by end plates coupled with tie rods. The pressure exerted by the tie rods is so great that totally reliable sealing is obtained in all the cells. A typical electrolyzer unit has an output capacity of from 110 to 750 standard cubic meters (or 4100 to 28,300 SCF) of hydrogen per hour. The delivery pressure is 30 kg/sq cm (or 440 psig). The electrolyte is 25% KOH, and the specific power consumption is from 4.3 to 4.6 kWhr per standard cubic meter of hydrogen (or 116 to 124 kWhr/1000 SCF of hydrogen). A typical plot of specific power consumption versus current for a cell with a diameter of 1.6-meter is shown in Figure 3-10.

According to staff at Lurgi, improvements in performance can be expected if they can find a way to increase the operating temperature of the cell. They believe that the factor limiting the temperature increase is the asbestos diaphragm. Researchers at Lurgi are also working on improved catalysts for the electrode structures, but information on these remains proprietary.

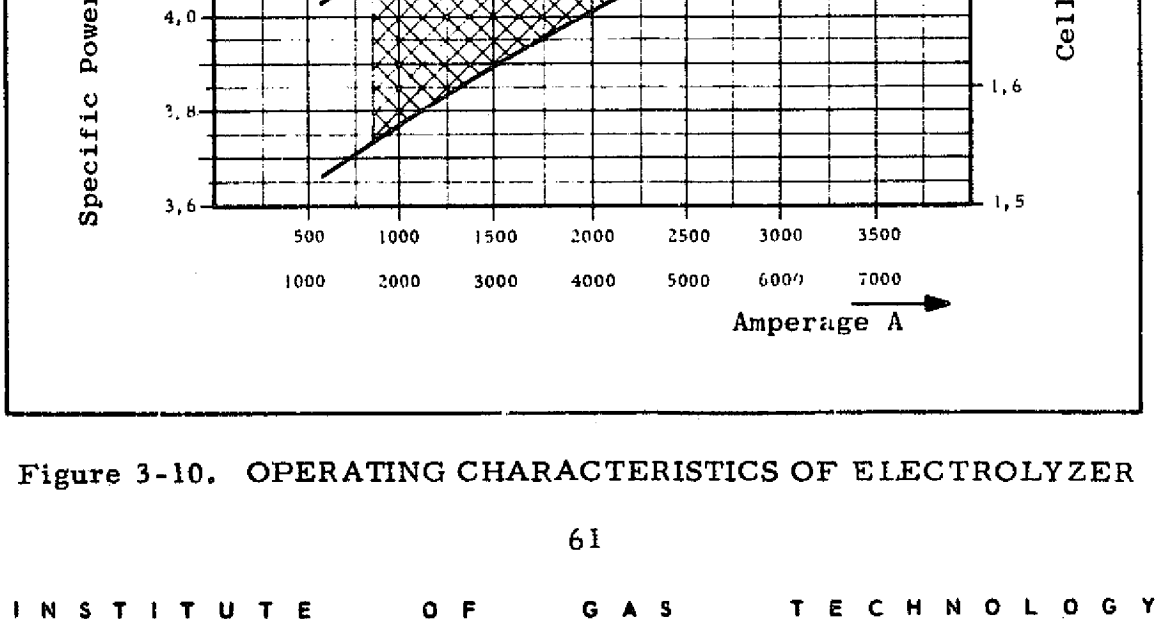


Figure 3-10. OPERATING CHARACTERISTICS OF ELECTROLYZER

A typical Lurgi high-pressure electrolyzer is shown in Figure 3-11.

Cominco, Ltd.[9,10]

One of the largest hydrogen plants in the world is located in Trail, British Columbia, Canada. Although it has been shut down for over a year now because of rising power costs, this plant represents the first North American attempt at large-scale hydrogen production.

Individual cells are of Cominco patented design. The characteristic feature of this tank-type cell is a concrete top that supports the electrodes, asbestos diaphragms, asbestos collecting skirt, feedwater pipes, bus bar, and gas-main connections. In this concrete cover also are the two gas chambers for hydrogen and oxygen and the narrow, inverted-trough-like collecting bins. The cell tank is made of iron, and the electrodes are made of mild steel plates. The anode is nickel-plated and has a current density of 67 A/sq ft.[15]

This hydrogen plant contains 3229 individual cells and has a total theoretical hydrogen-producing capacity of 41 tons of hydrogen/day. The cells operate at about 2.1 volts, the current efficiency is close to 100% at atmospheric operating pressure, ac-dc rectification is provided, and the overall ac power consumption is about 60,000 kWhr/ton of hydrogen.[10] At a usual operating temperature of 140°F, some cells have life spans of over 20 years.

De Nora, S.p.A.[1]

De Nora, S.p.A., of Milan, Italy, manufactures large, industrial, electrochemical processing plants that include the electrolysis of water in their range of applications. Of the three large electrolysis installations built since 1945, De Nora built the 1,059,300 CF/hr plant at Nangal, India. (The other two are a 2,118,600 CF/hr plant in Raikon, Norway, with its own Zdansky-type electrolyzers, and a 1,412,400 CF/hr plant at Kima, Egypt, built by Demag of Germany.) All these units are of bipolar, filter-press construction.

The standard De Nora electrolyzer[1] consists of rectangular cells 16.4 feet wide by 5.25 feet high. These are stacked in series on either side of a cooling chamber and are surmounted by an electrolyte gas separation unit. Figure 3-12 is a photograph of a typical cell stack.

A unique feature of the De Nora design is the use of a double diaphragm. Two distinct layers of woven asbestos are used. These are in physical contact with each other, but the space between them is vented to the atmosphere.

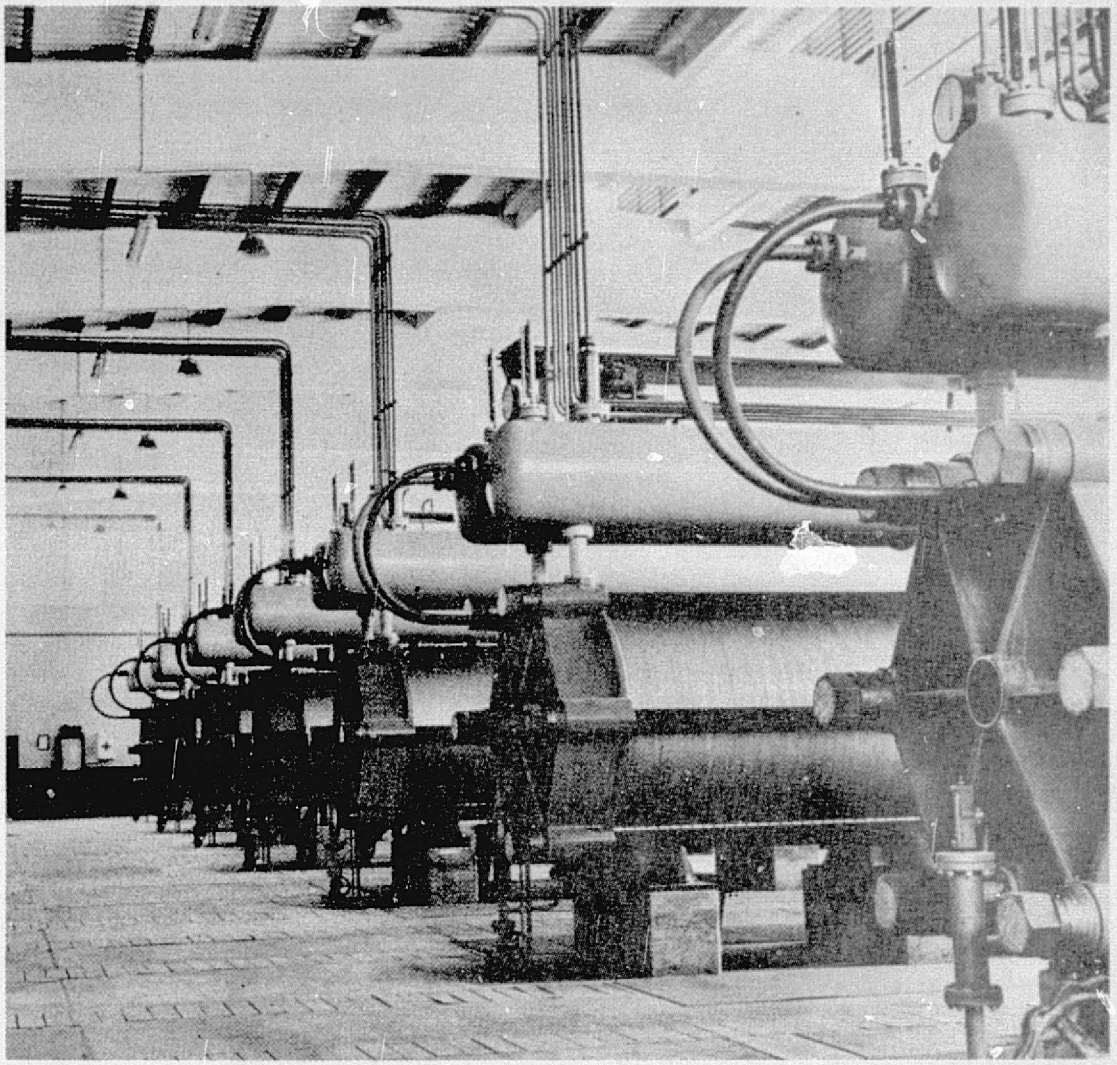


Figure 3-11. LURGI HIGH-PRESSURE ELECTROLYSIS PLANT (5100 Standard cu m of Hydrogen and 2550 Standard cu m of Oxygen per Hour)[8]

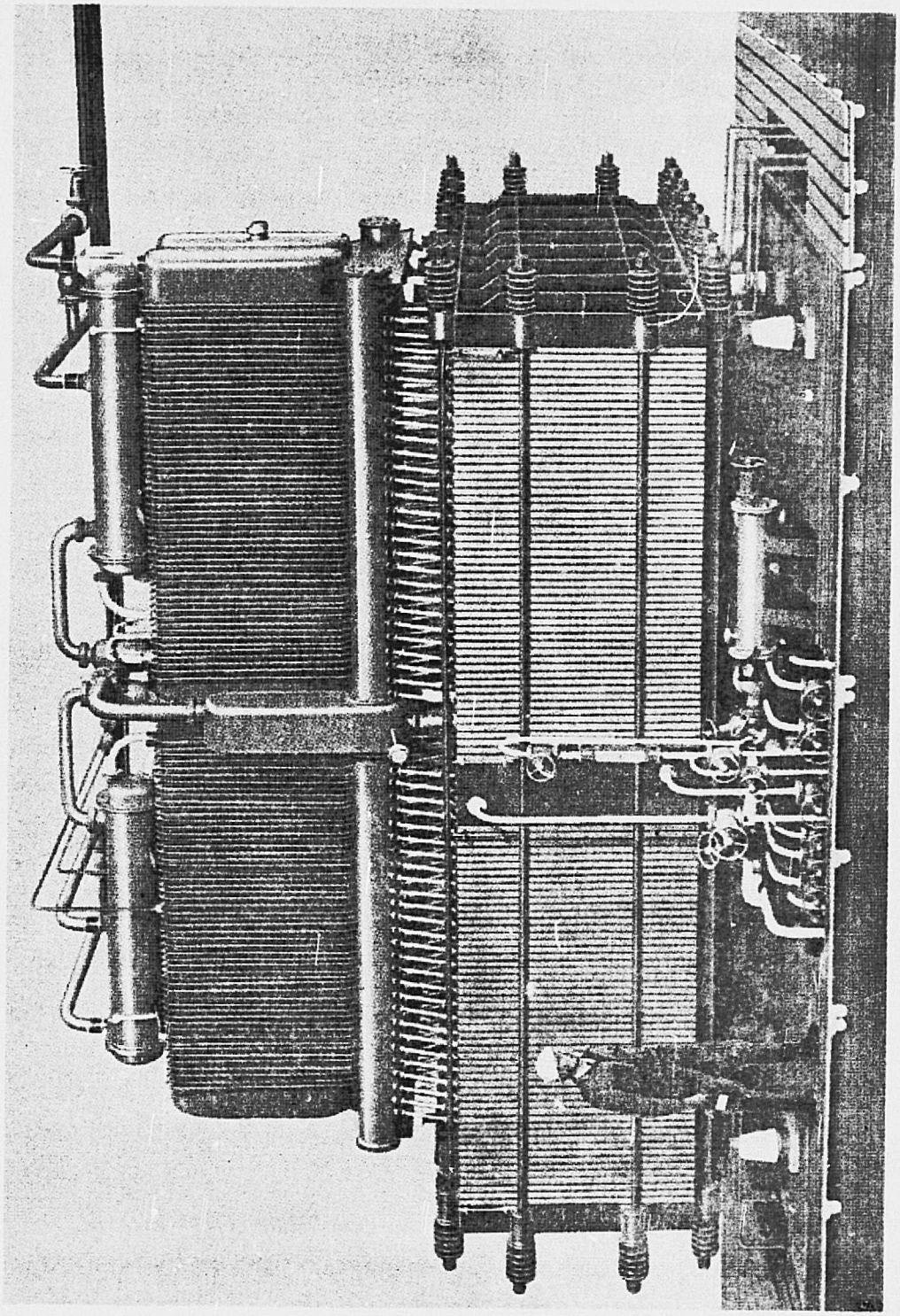


Figure 3-12. DE NORA WATER ELECTROLYZER[1]

During normal operation, the diaphragms are pressed against one another; but any penetration of gas bubbles results in the formation of a larger bubble between the diaphragms, which is then vented to the outside, and thus cannot intermix with the opposing gas.

The electrodes are single-layer sheet metal, perforated to allow gas to exit, and have a proprietary electrolytic surface treatment that creates a large surface area. No precious-metal catalysts are used. The electrodes are of low-carbon steel, and the anode is nickel-plated. The electrolyte is 25% KOH.

The Nangal plant consists of 60 units, each with 108 cells. Each cell stack is 16.4 x 5.25 x 49.2 feet in size and consumes 12,000 amperes at from 2.2 to 2.3 volts per cell (250 volts or 3 MW per unit). Thus, the entire plant consumes 180 MW (dc).

De Nora's standard cell sizes are 2500, 4500 and 10,000 ampere capacity and operate at about 180 to 200/sq ft. The Nangal plant, built in 1960, had a guaranteed performance of 2.1 volts per cell at 10,000 amperes. Any new plant delivered today would have a guaranteed performance of 1.85 volts at 12,000 amperes,[21] made possible by better activation treatment of the electrode. A performance of 1.80 volts at 18,000 amperes (300 A/sq ft) might be made possible by dissolving a homogeneous catalyst in the electrolyte, an approach that seems to be unique to De Nora.

Comparative Evaluation of Various Electrolyzers

Figure 3-13 is a comparison of the cell operating performances of various electrolyzers. These data are meant to give only a technological comparison of cell types, not a comparison of the economics; but a cell comparison based on voltage-current relationships is meaningless unless cell cost is included.

Interestingly, data for some advanced cell types are shown near and below the 1.47-volt point at current densities as high as 50 A/sq ft. Under these conditions, the cell operates "thermoneutrally," and the apparent thermal efficiency is 100%. This gives some reassurance that electrolyzer efficiencies approaching 100% can be achieved in practical units. At present, however,

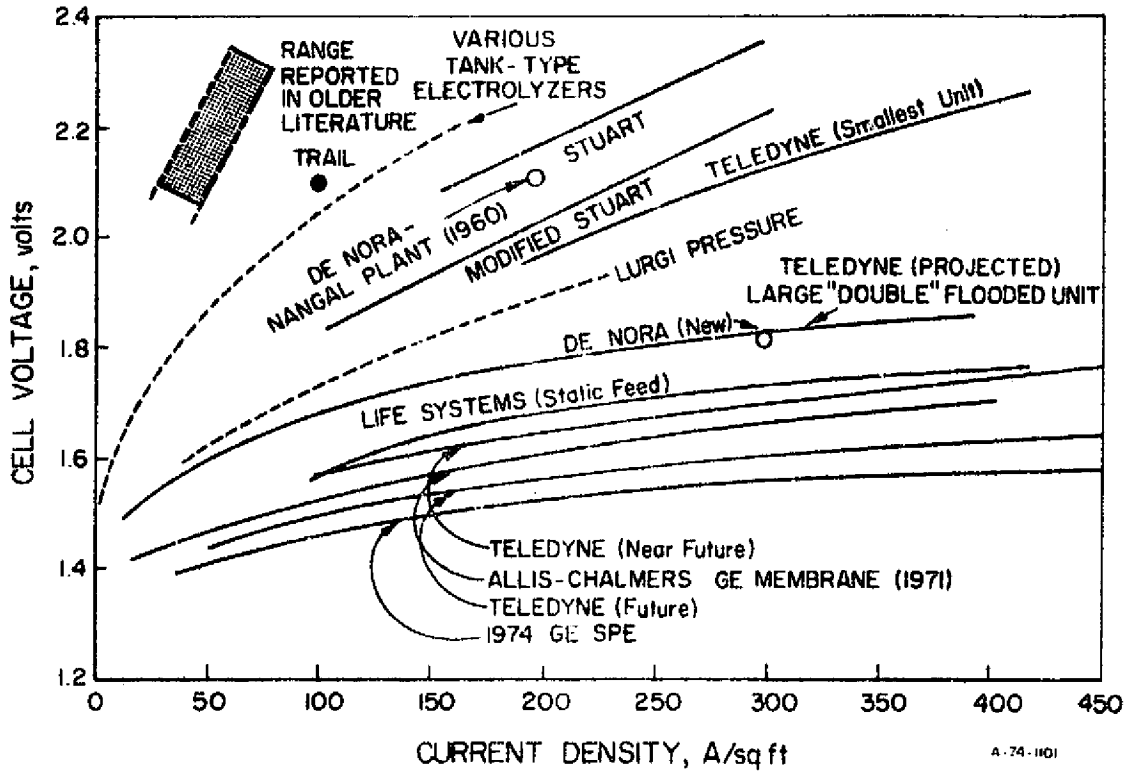


Figure 3-13. COMPARATIVE PERFORMANCE OF ELECTROLYZER SYSTEMS

operation of the GE cell at current densities below 1000 A/sq ft will cause proportionate increases in the effective capital cost.

Survey of Electrolyzer Manufacturers

Seven commercial manufacturers of fuel cells were contacted through either personal visits or correspondence. In addition, two chemical companies that manufacture and operate their own cells supplied limited information for the survey, as did one company that makes electrolyzers for space applications. (See Table 3-1). Manufacturers were asked to describe their systems, to provide data on cell performance and efficiency, and to provide enough cost information to enable us to derive the cost of hydrogen produced as a function of the amount of electric power supplied. It is noteworthy that a) manufacturers of the larger installations of electrolyzers are located in Europe, not in North America, b) very few of the manufacturers produce cells capable of delivering hydrogen at pressure, and c) most of the manufacturers prefer the stack or filter-press design to the tank type.

Table 3-1. MANUFACTURERS SURVEYED

Name	Location	Type	Pressure, psig
Electrolyser Corp.	Canada	Tank	0.4
Teledyne Isotopes, Inc.	U.S.A.	Stack	35-3000
De Nora, S.p.A.	Italy	Stack	1
Lurgi GmbH	W. Germany	Stack	440
Construction John Brown, Ltd.	U.K.	Stack	440-3000
Brown-Boveri	Switzerland	Stack	0.4
General Electric Co.	U.S.A.	Stack	2-3000
Norsk-Hydro	Norway	Tank	1
Cominco, Ltd.	Canada	Tank	0.1
Life Systems, Inc.	U.S.A.	Stack	600

Status of Industrial Electrolytic Hydrogen Production

Five large industrial electrolyzer plants (none in the United States) are currently producing hydrogen, for use in ammonia production, from hydroelectric power. In addition, many smaller units are located in almost every country in the world. These smaller units are used in applications in which high-purity hydrogen is required and in which operational manpower has to be kept to a minimum (See Table 3-2). Electrolytic hydrogen production is by no means the major way of producing hydrogen; but, on the other hand, it does represent a technology that is used to a significant extent in industry.

Electrolytic processes are widely used in industry, for other than hydrogen production; for example, most of the chlorine, caustic soda, and aluminum produced today are made by electrolytic processes. Process electrochemistry is thus a major arm of chemical technology.

Hydrogen Production by the Electrolysis of Impure Water

Electrolysis of Seawater

Seawater contains about 3.5% sodium chloride and smaller quantities of other dissolved salts. When a dilute sodium chloride solution is electrolyzed, various reactions are possible, including the following:

$$H_2O \rightarrow H_2 + 1/2\ O_2$$

and

$$2H_2O + 2NaCl \rightarrow 2NaOH + Cl_2 + H_2$$

Table 3-2. STATUS OF ELECTROLYTIC HYDROGEN PRODUCTION

Large Units

Location	Manufacturer	Hydrogen Output, 10^6 CF/hr	Power Input, MW	Year Built
Rjakon, Norway	Norsk-Hydro	2.2	250	1965
Kima, Egypt	Demag (BBC)	1.4(0.5)	170(60)	1960(1972?)
Nangal, India	De Nora, S.p.A.	1.1	125	1958
Trail, Canada	Cominco, Ltd.	0.7	90	1939
Curco, Peru	Lurgi GmbH	0.2	25	1958

Smaller Units

Many units in service used for —

- Fats and soaps
- Metallurgy
- Semiconductors
- Float glass
- Generator cooling
- Chemical feedstocks
- Meteorological stations

In practice, both reactions occur together; and, while hydrogen is evolved at the cathode, a mixture of oxygen and chlorine is evolved at the anode. This presents severely corrosive conditions at the anode and makes the selection of anode materials very critical. Moreover, the chlorine evolved presents a severe disposal problem, unless means of utilizing the chlorine can be found.

The conductivity of seawater is very low; and therefore, the resistance of the seawater electrolysis cell is too high for the process to be considered as a commercial means of hydrogen production. There are two potential ways of overcoming this problem. One is to concentrate the seawater into brine. The other is to add a supporting electrolyte, such as sodium hydroxide. In the first case, the partial dehydration of seawater to concentrated sodium chloride will result in the almost-complete suppression of the first, oxygen-evolving reaction and in the complete domination of the second, chlorine-producing reaction. Indeed, this is the process used in industry to produce chlorine and caustic soda in large quantities. In a chlorine-producing cell, means must be provided for removing the sodium hydroxide produced and for replacing the sodium chloride. Although this type of cell does, in fact, produce large quantities of hydrogen, its use as a primarily hydrogen-producing cell is not feasible because of the large amounts of byproducts. If hydrogen is to be produced in the quantities that are of interest for large-scale chemical feedstocks and fuels, then the disposal of both the sodium hydroxide and the chlorine presents serious problems.

The other alternative, the addition of sodium hydroxide as a supporting electrolyte, is only slightly more attractive. As the cell is operated, it produces its own sodium hydroxide; therefore the concentration of this electrolyte will automatically increase to a point at which the sodium hydroxide itself must be dumped from the cell. If the concentration of sodium chloride can be kept low, the evolution of chlorine can be kept to a minimum and, in principle, the cell could be retained as a hydrogen-oxygen cell. However, because the cell is only expelling hydrogen and oxygen with an intermediate purging of sodium hydroxide and because it is constantly being fed a sodium chloride solution, the chloride-ion concentration inevitably builds up in the cell. This ultimately results in an increase in chlorine evolution, resulting in the same problems as have previously been discussed.

We conclude that the electrolysis of seawater to produce hydrogen alone is not a practical proposition, and research in this area does not appear to be justified.

Electrolysis of Unpurified Water

The electrolysis of water that contains only small levels of impurities results in the production of hydrogen and oxygen, but also in the continual accumulation of the impurities in the cell. This occurs because the cell is only able to produce hydrogen and oxygen; and if even the smallest amounts of impurities are present in the water fed to the cell, these impurities cannot escape from the cell and ultimately reach a high degree of concentration. The results of the accumulation of impurities include: 1) corrosion of the electrodes, 2) the onset of side reactions that give rise to undesirable byproducts, and 3) contamination of the ion-exchange membrane in the SPE-type cell. Inhibiting the accumulation of impurities by purging the electrolyte in the cell does not appear to be an attractive solution because of the cost of the continual replenishment of the KOH electrolyte. Thus, there does not seem to be a reasonable prospect for the economic electrolysis of impure water as long as water-purification costs remain reasonably low.

Electrolyzer-Feedwater Quality Standards

Most electrolyzer manufacturers stipulate feedwater quality in their specifications. In general, feedwater must be purified to a level approximating that of boiler-feedwater quality or "distilled-water" standards. Most electrolyzers have demineralizers in the feedwater stream that remove the last traces of dissolved salts. Thus the electrolyzer can be fed replacement water continuously for periods of up to 6 months. Lurgi specifies feedwater of an initial purity equivalent to that of heating-steam condensate, the feedwater then being passed through an active carbon filter and through a demineralization unit containing a mixed-bed ion exchanger that provides the water with a minimum specific resistance of 1 megohm-centimeter. Usually, the purity of the feedwater is monitored by a conductivity meter installed in the system.

Energy Required for Water Purification

Upon first consideration, the requirements for a pure-water feed may appear to be prohibitively expensive. However, the amount of water required to feed an electrolyzer is relatively small compared with the amount of hydrogen pro-

duced. For example, the electrolysis of 1000 gallons of water will produce 166,000 SCF of hydrogen. Thus both the energy cost and the dollar cost of treating 1000 gallons of water should be debited from the selling price of the 166,000 SCF of hydrogen produced. The latent heat of vaporization (or the energy required for straight distillation) is 9.8 kcal/mole, while typical water desalting methods appear to use between 1 and 10 kcal/mole.* This is to be compared with the typical electrical input, 93 kcal/mole, to the commercial electrolyzer operating at 2 volts. Thus the energy required for water purification is 10% or less of the electrical energy required for the electrolysis itself. The energy required to desalt water is of a far lower grade than that needed to run an electrolysis plant, which of course has to be in the form of electricity. Relatively low grade heat, possibly available from the power station supplying the electricity, could be used to purify the electrolyzer feedwater.

The cost of desalting seawater to irrigation standards was earlier estimated at approximately $0.80/1000 gal. The 1000 gallons would, in turn, produce 166,000 SCF of hydrogen; thus the ratio of the water desalting cost to the heating value of the hydrogen produced would be about 1.4¢/million Btu. This is considerably less than 1% of the expected selling price of the hydrogen. It is likely that the full treatment of seawater to the 1 megohm-centimeter standard required by an electrolyzer will in fact costmore than $0.80/1000 gal; but in any event, the overall cost of purifying the water is likely to be less than 2% or 3% of the anticipated overall cost of producing the hydrogen.

We conclude, then, that rather than embarking on a research program to solve the difficult problems of electrolyzing sewater or brackish water, it is better to suffer the small energy and cost penalties involved in purifying the water to acceptable standards.

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* Recent technology indicates[6] that a multiple-effect distillation system has an energy requirement of 1 million Btu/1000 gal, or approximately 1.2 kcal/g-mole.

Note that any process that converts water to hydrogen and oxygen is likely to require the same consideration of feedwater standards. Any process that splits water into hydrogen and oxygen will deposit feedwater impurities, thus contaminating the plant. It is therefore anticipated that thermochemical processes, as well as electrochemical processes, will require water-treatment plants and therein incur a similar expense.

References Cited in This Section

1. De Nora, S.p.A., De Nora Water Electrolyzer, Milan, Italy, n.d.

2. General Electric Co., Aircraft Equipment Division, "Hydrogen Generator for Gas Chromatographs," Publ. DEC-3-74-1. Lynn, Mass., December 1974.

3. Jensen, F. C. and Schubert, F. H., "Hydrogen Generation Through Static Feedwater Electrolysis." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami Beach, March 18-20, 1974.

4. Kincaide, W. C., Teledyne Isotopes, Inc., private communication of May 10, 1973.

5. Kincaide, W. C. and Williams, C. F., Storage of Electrical Energy Through Electrolysis, p. 15. Timonium, Md.: Teledyne Isotopes, Inc., 1973.

6. Kremen, S. S., "Reverse Osmosis Makes High-Quality Water Now," Environ. Sci. Tech. 9, 314-18 (1975) April.

7. Laskin, J. B., "Electrolytic Hydrogen Generators." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami Beach, March 18-20, 1974.

8. Lurgi GmbH, "Hydrogen From Water," Express Inf. T1084/6173, Frankfort, Germany, 1973.

9. Robinson, J. N., Cominco Ltd., private communication of January 26, 1971.

10. Ross, M., Cominco Ltd., private communication of May 29, 1974.

11. Russell, L. H., Nuttall, L. I. and Fickett, A. P., "Hydrogen Generation by Solid-Polymer-Electrolyte Water Electrolysis." Paper presented to the American Chemical Society, Division of Fuel Chemistry, Chicago, August 1973.

12. Schubert, F. H., Status of the Life System's Static Feedwater Electrolysis System. New York: The American Society of Mechanical Engineers, July 1971.

13. Stuart, A. K., "Modern Electrolyser Technology." Paper presented at the American Chemical Society Symposium on Nonfossil Fuels, Boston, April 15, 1972.

14. Stuart, A. K., The Electrolyser Corp., private communication of June 11, 1974.

15. Sutherland, B. P., "Electrolytic Hydrogen Cells of Frail Design." Paper presented at the Electrochemical Society Meeting, Milwaukee, April 17, 1974.

16. Teledyne Isotopes, Inc., Hydrogen Oxygen Gas Generator Systems, Timonium, Md., n. d.

17. The Electrolyser Corp., Electrolytic Hydrogen Plants and Generators, Toronto, n. d.

18. Titterington, W. A., "Status of GE Company SPE Water Electrolysis for Hydrogen-Oxygen Production." Paper presented at the World Energy Systems Conference, Hurst, Texas, June 9, 1974.

19. Titterington, W. A., General Electric Co., private communication of June 10, 1974.

20. Titterington, W. A. and Ficket, A. P., "Electrolytic Hydrogen Fuel Production With Solid Polymer." Paper presented at the Eighth Intersociety Energy Conversion Conference, Philadelphia, August 13, 1973.

21. Trisoglio, G., DeNora, S. p. A., private communication of June 28, 1974.

22. Wullenweber, H., Lurgi GmbH, private communication of February 1975.

4. COST OF ELECTROLYTIC HYDROGEN — K. G. Darrow, Jr.

The basis for the costs contained in this section is information supplied by three major vendors of electrolysis systems. We contacted several such companies by mail and/or in person and requested technical and economic data regarding capital costs, operating parameters, scale-up factors, and polarization curves. The General Electric Co., Lurgi Apparate-Technik of Germany, and Teledyne Isotopes each supplied us with enough information to allow for an estimate of overall capital and operating costs.

Factors Considered in Overall Hydrogen-Cost Calculations

With the data provided by the manufacturers, we were able to calculate the cost of electrolytic hydrogen production as a function of electric power. Such curves for electrolysis systems have appeared in much of the recent literature concerning hydrogen, but there has been no uniform base for determining these costs. Different financial assumptions can lead to very different figures for the cost of hydrogen, even when utilizing the same equipment. Some vendors include more equipment within their quoted costs than do others. At the same time, certain systems need more auxiliary equipment than do others. Although the information received from the vendors was not complete in all cases, we have attempted the analysis of a standard-sized plant producing 10 million SCF/day of hydrogen. Respecting the proprietary nature of the information provided and market position of the respondents, we have elected to somewhat limit the degree of detail presented in this section.

To provide a clear idea of all that is involved in building a large-scale electrolysis plant, the equipment and auxiliary facilities of a typical alkaline-electrolyte, "filter-press" design system are given below. The major equipment components of such a system are —

- Electrolyzer modules
- Gas separators
- Gas cooling system
- Electrolyte cooling system
- Feedwater supply system
- Electrolyte preparation and storage tank
- Nitrogen tank and purge system.

Also required, and generally included by the vendor as part of the equipment cost, are —

- Pumps and pump motors
- Instrumentation and control facilities
- Maintenance equipment
- Valves and piping.

If any of these items are not included as part of the quoted equipment costs, they must be added to the overall plant costs.

In addition to the cost of plant equipment, the costs of the following items and services must be added to the investment to derive the cost of a complete facility:

- An electrical plant consisting of ac-to-dc rectification and transformers
- Packing, shipping, and installation of the equipment
- Additional electrical equipment and its installation, (e.g., bus bars, switches, cables)
- A building, foundation, and other support structures, including lighting and painting
- Facilities for services such as water treatment, water distribution, air compression, communications, and fire protection
- Engineering and supervision during construction and start-up
- Contractors
- Land, site preparation and yard improvements, and administrative facilities.

Finally, compression, transmission, and storage costs, which are developed separately in this report, must be included. This section, however, is devoted solely to production costs.

To indicate the magnitude of the additional costs that must be added to the equipment costs, we have developed factors for these other items based on percentages of equipment costs reasonable for chemical processes in general and for specific electrolytic plants. Table 4-1 presents two cost work-ups — one for a pressurized alkaline cell that represents a composite of Lurgi and Teledyne information for currently available equipment and the other for the

Table 4-1. CAPITAL COSTS FOR ELECTROLYSIS PLANTS

Equipment Costs	Alkaline Pressure Electrolyzer $/kW (out)*	Projected GE 1980 Commercial $/kW (out)
Electrolyzer and Auxiliary	255	84
Power Conditioning ($45/kW ac in)	60	57
Total	315	141
Installed Plant Cost		
Equipment X 1.5	472/kW (out)	212/kW (out)

* $/kW (out) = dollars per kilowatt of product hydrogen, converted on the basis of higher heating value; i.e.—

$$\frac{\text{Capital Cost}}{\text{SCF/hr X 325 Btu/SCF} \div \text{3413 Btu/kWhr}}$$

The fact that the GE cell will operate at about 10 times the current density of the alkaline cell explains its relatively low cost (on an equivalent output basis), in spite of the fact that the GE cell actually uses more expensive materials than the alkaline cell.

reported GE Solid-Polymer Electrolyte (SPE) system that is to be developed by 1977 and commercialized by 1980. The percentages quoted for GE installations are higher (that is, the auxiliary-equipment costs for the GE system are a greater percentage of the total capital cost) because GE's cells are expected to be cheaper (on a unit-output basis) than currently available cells, but the costs of their auxiliary equipment will be about the same as for present-day cells.

The accuracy of this kind of cost projection is on the order of plus or minus 30%. However, the information on overall costs for large-scale water electrolysis systems is scanty, at best. Although such systems have been built, typically they are few in number; were built as many as, or more than, 20 years ago; and were built in nonindustrial areas, and cost breakdowns were never published.

Table 4-2 summarizes the system operating characteristics reported by the three responding companies. Where information was lacking, we were forced to make assumptions, often based on information supplied by other vendors. Because the cost of electric power is the most important operating cost, we have assigned fixed values to all other operating costs and have computed the hydrogen costs parametrically as a function of electrical costs. Other operating costs are shown below in order of their importance:

1. Maintenance, 2% of total investment
2. Cooling-tower water, 15¢/1000 gal
3. Direct labor (2 persons per shift), 8.4 person-years at $6.00/hr
4. Overhead, 50% of direct labor
5. Demineralized feedwater, 1 megohm-cm minimum resistance, $1.90/1000 gal.

In addition to these operating costs, capital charges representing depreciation, income taxes, interest on debt, return on equity, and ad valorem taxes and insurance must be taken into account. We adopted a straightforward financing method in an attempt to represent an average utility situation. The parameters we used are as follows:

- 60:40 debt-to-equity ratio
- 4% interest on debt

Table 4-2. OPERATING CHARACTERISTICS OF THREE ELECTROLYZERS

	Teledyne	Lurgi	GE (Projected)
Size of System Compared, MW equivalent of hydrogen	39.9	53.3	51.6
Million SCF of Hydrogen/ Stream Day	10	13.44	13.0
DC Electric Input (Max.), kW	58,400	69,000	65,300
Specific Cell Efficiency	68%-70%	77%	82.2
AC-DC Converter Efficiency	86%	97%	97%
Auxiliary-System Efficiency		NA	99%
Overall Efficiency	58.7-60.4	74.7	78.9
Operating Pressure	100 psig	440 psia	Pressure vessel designed for operating pressures of up to 3000 psig
Cooling Water, gal/hr	NA	184,940	Closed cycle, dry cooling tower
Feedwater, gal/1000 SCF	6.36	6.36	6.36
Nitrogen per Start-up	Yes	74,640 SCF	No
Caustic-Potash Initial Charge, lbs	NA	344,000	None
Labor, men/shift	NA	2	NA
Mode of Operation	Fully automatic	Fully automatic	Fully automatic

Note: NA = not available.

- 15%, after tax, return on equity
- 48% income-tax rate with no investment tax credits
- 20 years' sum of year's digits depreciation on total plant investment, for taxes, and 20 years' straight-line depreciation, for cost accounting. (Note that all three vendors specified a 20-year life.)

The weighted average cost of capital for this capital structure is 11.4%. The annual fixed-charge rate that would exactly yield this return for the overall firm was computed to be 18.6%, the sum of a capital-recovery factor of 12.8%, an income-tax factor of 3.8%, and an allowance of 2% for ad valorem taxes and insurance.

We then developed a unit hydrogen cost that satisfies the minimum revenue requirements of the firm – i.e., it covers all operating costs and yields a return on investment equivalent to the cost of capital. Figures 4-1 and 4-2 show hydrogen costs (as a function of electricity rates) for systems functioning at a 90% plant-operation factor – 10% of the total possible operating time having been set aside from the otherwise continuously run system to allow for downtime for scheduled maintenance. (Note that Figure 4-1 is based on present-day cells while Figure 4-2 is a projection based on the expected 1980 technology.)

Optimization of Operating Characteristics

It should be pointed out that the operating characteristics of a given electrolyzer can be "tuned" to provide hydrogen at the minimum cost possible under a given set of economic conditions. This is one reason for some vendors' reluctance to make generalized cost statements.

The hydrogen output of a given electrolyzer varies directly with the current applied to the cell (based on the relationship of 15.6 SCF of hydrogen/1000 A-hr). However, as the current density on the electrodes is increased, efficiency decreases. Hence, as current density is increased, unit capital costs decrease and electric power requirements increase. At some current density, hydrogen costs will be minimized.

The point of minimum cost is determine by describing capital costs and efficiency as functions of current density and by then substituting these functions into the overall cost equation. The partial derivative of the cost equation with respect to current density is then used to find the point of minimum cost.

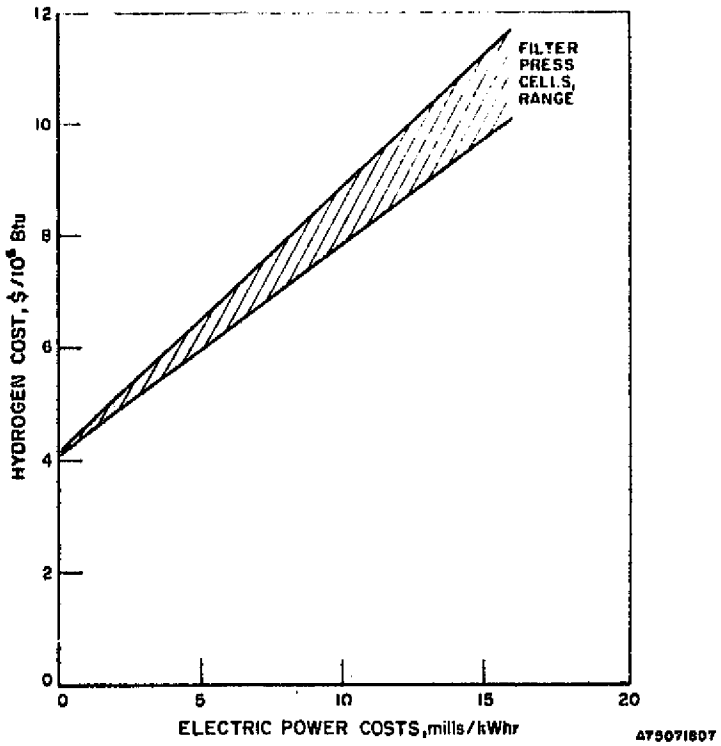


Figure 4-1. HYDROGEN COSTS VS. ELECTRICITY RATES FOR PRESENT-DAY CELLS

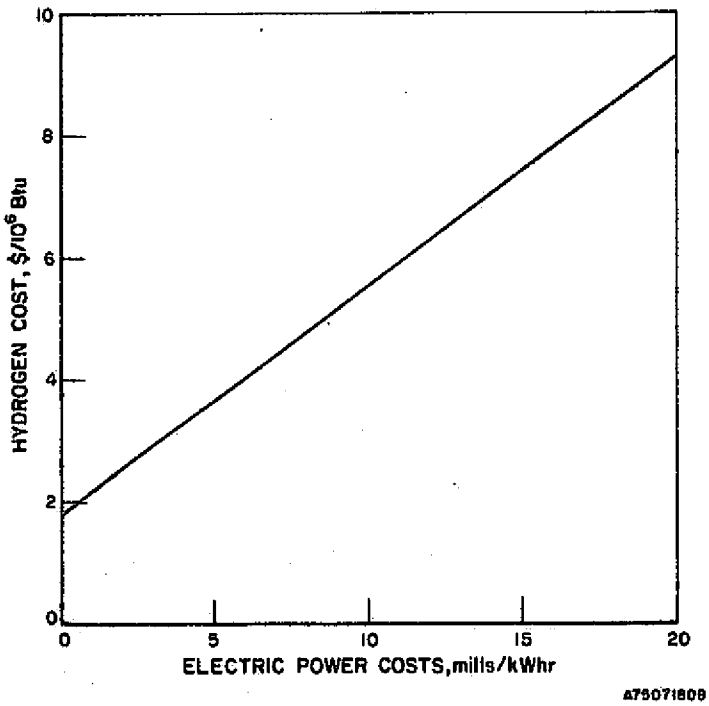


Figure 4-2. HYDROGEN COSTS VS. ELECTRICITY RATES FOR GE ELECTROLYZER (1980 Projection)

Plant life, however, is also a function of current density. In our analysis, plant life was assumed constant, with the added constraint that current density not exceed the manufacturer's recommended maximum value.

Any conclusions drawn from an inspection of Figure 4-1 and 4-2 are true only for the situation described by our technical and economic assumptions. Any other assumptions could conceivably change the relative positions of these curves.

It should be noted that comparatively large industrial units are, today, available for purchase from some manufacturuers while others represented in this figure are, at present, unable to meet large industrial orders. Thus, in some cases this figure compares current selling prices with projected prices.

5. THE MANUFACTURE OF HYDROGEN FROM COAL — C. L. Tsaros, J. Arora, and K. B. Burnham

As part of the NASA-Langley Research Center project being conducted by IGT, process flow diagrams for the conversion of coal to high-purity hydrogen were prepared and are herein presented. The process flow diagrams, energy balances, and efficiencies reported herein are preliminary, and the reader is referred to the NASA-LRC report* for finalized information. Plant capacities that would yield total product heating values of 250 billion Btu/day were established. Because of small variations in product heating value, production rates range from 698 to 767 million SCF/day. This capacity is typical for the standard methane- or pipeline-gas-from-coal plant and is considered to be beyond the point at which economy of scale is significant. It also meets the supply required by a major airport for aircraft fueling.

Processes were selected purposely to represent different technologies. Process designs have been made in sufficient detail to allow determination of overall plant efficiencies on a comparable basis. In addition, capital and operating costs for one of the processes were estimated for comparison with the costs of methane and kerosene produced from coal, as estimated in other phases of the project. The processes selected are —

- The Koppers-Totzek Process — a commercially available process based on the suspension gasification of pulverized coal by steam and oxygen at essentially atmospheric pressure under slagging conditions in excess of 3000°F. Since the first commercial installation of the Koppers-Totzek Process in Oulu, Finland, in 1952, 20 plants have been ordered that use a total of 52 Koppers-Totzek gasifiers. Four of these plants were ordered after 1970. The most common use of the product gas has been for ammonia synthesis. A hydrogen-production facility would utilize the same gasifying principles as an ammonia plant, but would require different downstream process operations, which are described in this report. A complete list of the 20 commercial installations, none of which is in the United States, is presented in Table 5-1.

* Tsaros, C. L., Arora, J. and Burnham, K. B., "Study of Conversion of Coal to Hydrogen, Methane, and Liquid Fuels," IGT Project 8963, Contract NAS 1-13620, Chicago, 1975.

Table 5-1. COMMERCIAL PLANTS FOR GASIFICATION OF ALL KINDS OF FUELS BY THE KOPPERS-TOTZEK PROCESS

Plant	Fuel	Number of Gasifier Units	Capacity (Carbon Monoxide and Hydrogen in 24 hr) standard cu m	SCF	Use of Synthesis Gas	Year of Order
African Explosives and Chemical Industries Ltd., Johannesburg, Modderfontein Plant, South Africa	Coal dust	6	2,150,000	80,025,000	Ammonia synthesis	1972
Amoniaco Português S.A.R.L., Lisbon, Estarreja Plant Portugal	Heavy gasoline, plant extendable to lignite- and anthracite-dust gasification	2	169,000	6,300,000	Ammonia synthesis	1956
Azot Sanayii T.A.S., Ankara, Kütahya Works, Turkey	Lignite dust	4	775,000	28,850,000	Ammonia synthesis	1966
Charbonnages de France, Paris, Mazingarbe Works (P.d.C.) France	Coal dust, coke-oven gas, tail gas	1	75,000-150,000	2,790,000-5,580,000	Methanol and ammonia synthesis	1949
Chemical Fertilizer Company Ltd., Thailand, Synthetic Fertilizer Plant at Mae Moh, Lampang, Thailand	Lignite dust	1	217,000	8,070,000	Ammonia synthesis	1963
Chemieanlagen Export-Import GmbH, Berlin für VEB Germania, Chemieanlagen und Apparatebau Karl-Marx-Stadt VEB Zeitz Works	Vacuum residue and/or fuel oil	2	360,000	13,400,000	Raw gas to produce hydrogen for hydrogenation	1966
Empresa Nacional "Calvo Sotelo" de Combustibles Liquidos y Lubricantes, S.A., Madrid, Nitrogen Works in Puentes de Garcia Rodriguez, Coruña, Spain	Lignite dust	3	242,000	9,000,000	Ammonia synthesis	1954
Empresa Nacional "Calvo Sotelo" de Combustibles Liquidos y Lubricantes, S.A., Madrid, Nitrogen Works in Puentes de Garcia Rodriguez, Coruña, Spain	Lignite dust or naphtha	1	175,000	6,500,000	Ammonia synthesis	1961
Kobe Steel Ltd., Kobe Japan for Industrial Development Corp., Zambia, at Kafue Near Lusaka Zambia, Africa	Coal dust	1	214,320	7,980,000	Ammonia synthesis	1967
Nihon Suiso Kogyo Kaisha, Ltd., Tokyo, Japan	Coal dust	3	210,000	7,820,000	Ammonia synthesis	1954
Nitrogenous Fertilizers Industry S.A., Athens, Nitrogenous Fertilizers Plant Ptolemais, Greece	Lignite dust	1	165,000	6,150,000	Ammonia synthesis	1969
Nitrogenous Fertilizers Industry S.A., Athens, Nitrogenous Fertilizers Plant Ptolemais, Greece	Lignite dust	1	242,000	9,009,000	Ammonia synthesis	1970
S.A. Union Chimique Belge, Brussels, Zandvoorde Works Belgium	Bunker-C oil, plant convertible for coal-dust gasification	2	176,000	6,550,000	Ammonia synthesis	1955
The Fertilizer Corporation of India Ltd., New Delhi, Korba Plant, India	Coal dust	4 (One as standby)	2,000,000	74,450,000	Ammonia synthesis	1972
The Fertilizer Corporation of India Ltd., New Delhi, Ramagundam Plant, India	Coal dust	4 (One as standby)	2,000,000	74,450,000	Ammonia synthesis	1969
The Fertilizer Corporation of India Ltd., New Delhi, Talcher Plant, India	Coal dust	4 (One as standby)	2,000,000	74,450,000	Ammonia synthesis	1970
The General Organization for Excuting the Five Year Industrial Plan, Cairo, Nitrogen Works of Société el Nasr d'Engrais et d'Industries Chimiques, Attaka, Suez, United Arabian Republique	Refinery off-gas, LPG, and light naphtha	3	778,000	28,950,000	Ammonia synthesis	1963
The Government of the Kingdom of Greece, The Ministry of Coordination, Athens: Nitrogenous Fertilizers Plant, Ptolemais, Greece	Lignite dust, bunker-C oil	4	629,000	23,450,000	Ammonia synthesis	1959
Typpi Oy Oulu, Finland	Coal dust, oil, and peat	3	140,000	5,210,000	Ammonia synthesis	1950
Typpi Oy Oulu, Finland	Coal dust, oil and peat	2	140,000	5,210,000	Ammonia synthesis	1955

- The U-GAS™ Process — currently undergoing process development on a fluidized-bed gasifier. The operating pressure is substantially above atmospheric, 300 psig being typical. Gasification occurs in the presence of steam and oxygen, but under nonslagging conditions at 1900° F. The U-GAS Process is primarily intended to produce a low-Btu fuel gas. A 4-foot-diameter gasifying reactor is now in operation. The project is jointly funded by the Energy Research and Development Administration and the American Gas Association as part of the IGT HYGAS program.

- The Steam-Iron Process — a modern, continuous version of the old batch method of generating hydrogen. To make a producer gas, coal is gasified by steam and air in a fluidized bed at 1900° F. This gas is used to regenerate iron oxide, which, in the reduced state, decomposes steam in a separate vessel to provide the hydrogen. The iron oxide is circulated between the oxidizer (hydrogen-generation vessel) and the reductor. Because the hydrogen is not derived from the producer gas, the nitrogen introduced in the use of air does not contaminate the product. The new process is designed to operate at a pressure of 350 psi, which allows for smaller reactors than does the old, atmospheric-pressure batch process. This modern system is being developed at IGT to supply hydrogen for the HYGAS Process. Construction of a continuous steam-iron pilot plant has begun.

The above processes produce hydrogen ranging in purity from 93% to 96%, the impurities being nitrogen and methane (produced in the gasifier). Because of variations in the methane/nitrogen proportions, there are small variations in heating value.

250 Billion Btu of Hydrogen per Day From Montana Subbituminous Coal by the Koppers-Totzek Process

The Koppers-Totzek Process involves the partial oxidation of pulverized coal in suspension with oxygen and steam. (This design is based on the gasification of Montana subbituminous coal.) The conversion of coal to hydrogen is a complex process that requires many operations. These may be grouped under three major headings:

1. Coal storage and preparation
2. Coal gasification for production of synthesis gas
3. Upgrading of the raw synthesis gas to produce hydrogen.

Figure 5-1 is a flow diagram of the processing steps required for this plant.

Coal Storage and Preparation

The hydrogen plant is assumed to be located near a coal mine that will provide coal for at least 25 years. Raw coal is brought, by truck, from the

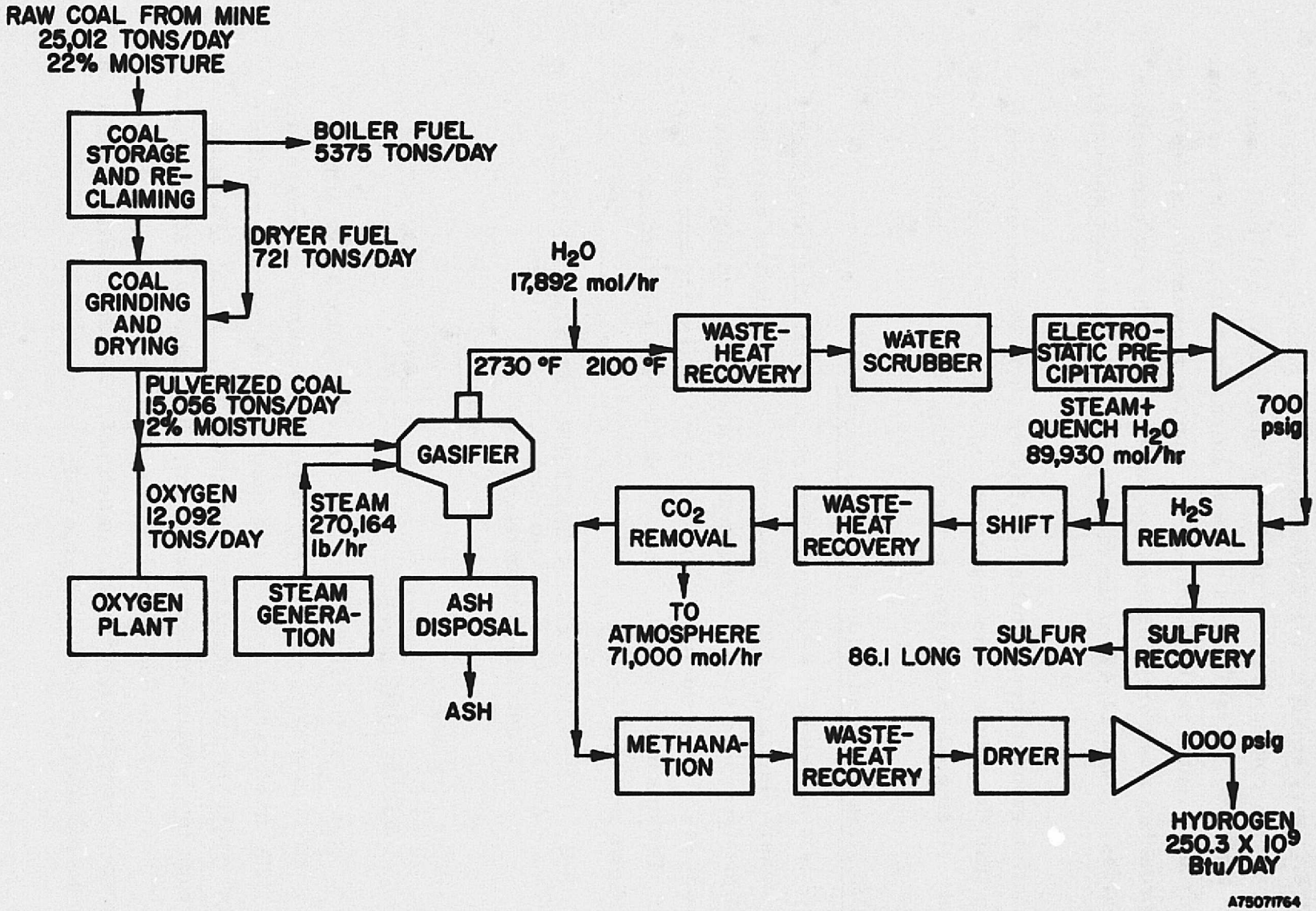


Figure 5-1. KOPPERS-TOTZEK GASIFICATION FOR A 250 X 10^9 Btu/DAY HYDROGEN PLANT THAT USES MONTANA SUBBITUMINOUS COAL

mine to a storage area where a 60-day supply of coal (broken to 1-1/2-inch x 0 size — i.e., very small to 1-1/2-inch-diameter pieces) is accumulated. The plant requires a continuous flow of 25,012 tons of raw coal (22% moisture) per day from the mine. Provision is made to store the coal in such a way that it is uniformly distributed in the storage pile; and the reclaimed coal fed to the gasifiers approaches a uniform composition, even though the run composition of the coal varies. About 24.4% of the feed coal is used as boiler and dryer fuel.

In combination grinder-dryer mills, coal is dried to 2% moisture and is pulverized so that 70% of the mass passes through 200 mesh (74-micron opening). The pulverized coal is conveyed to the storage bins before being fed to the gasifiers.

Coal Gasification for Production of Synthesis Gas

Figure 5-2 is a sketch of the Koppers-Totzek gasifier. The pulverized coal is continuously discharged into a mixing nozzle in which it is entrained in oxygen and low-pressure steam. Moderate temperature and high burner velocity prevent reaction of the coal with the oxygen until entry into the gasification zone. The quantities of coal, steam, and oxygen required for the gasifier are shown in Table 5-2.

Table 5-2. KOPPERS-TOTZEK GASIFIER FEED QUANTITIES
(For a 250 X 10^9 Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Amount
Coal, lb/hr (dry basis)	1,229,590
Steam, lb/hr	270,164
Oxygen, tons/day (98% pure)	12,092

The oxygen, steam, and coal react at a pressure slightly above atmospheric and at 3300°F in a refractory-lined, horizontal cylindrical vessel with conical ends. The fixed carbon and volatile matter in the coal are gasified to produce raw synthesis gas and molten slag at 2730°F. About 50% of the molten slag drops into a water-filled quench pot, thus forming a 200°F slag-water slurry. This slurry is cooled to 125°F and is sent to a slag-settling pond. The water is recycled to the slag quench pot. The composition of the raw gas from the gasifier is shown in Table 5-3.

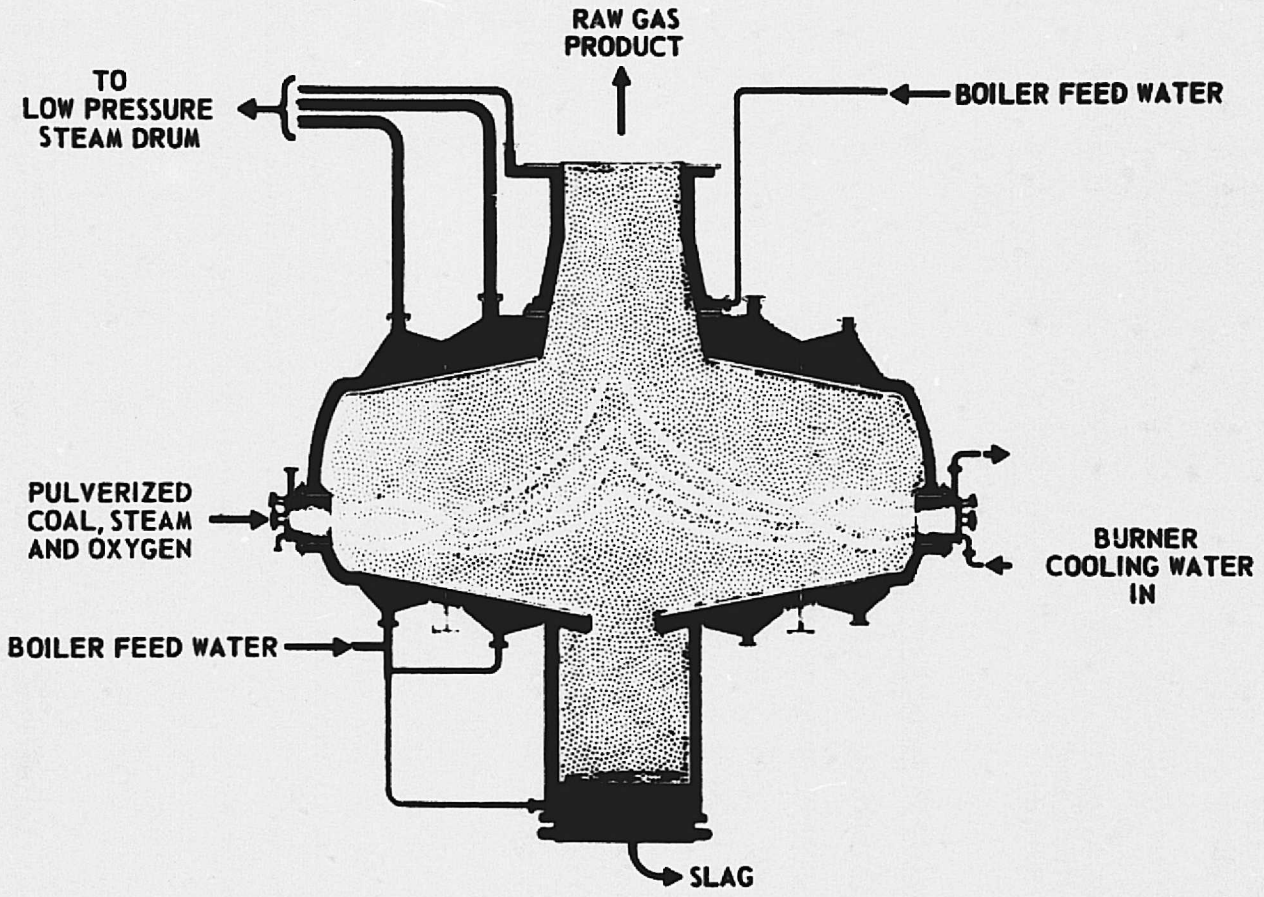


Figure 5-2. KOPPERS-TOTZEK GASIFIER

Table 5-3. COMPOSITION OF THE RAW GAS FROM A KOPPERS-TOTZEK GASIFIER
(Pressure, 6.2 psig; Temperature, 2730°F)

	Actual mole %	Dry Basis mole %
Carbon Monoxide	51.3	58.3
Carbon Dioxide	8.8	10.0
Hydrogen	26.8	30.4
Water Vapor	12.0	--
Methane	--	--
Nitrogen and Argon	0.9	1.0
Hydrogen Sulfide and Carbonyl Sulfide	0.2	0.3
Total	100.0	100.0

Upgrading of the Raw Gas to Produce Hydrogen

The synthesis gas leaving the gasifier is cooled to 2100°F by direct quenching with water, which also helps to solidify the entrained slag droplets. The quenched gas is cooled to 180°F in the waste-heat recovery boiler where a significant portion of the 1200-psig, 900°F, superheated steam for driving the turbines is generated. The cooled gas is washed with water in a venturi scrubber to reduce entrained solids to a concentration of between 0.002 and 0.005 grains/SCF. The gas is cleaned further, in electrostatic precipitators, before it is compressed to 700 psig. The slag and fine particles removed in the venturi scrubber are disposed of.

In order to upgrade the gas to the desired hydrogen product, the dust-free compressed gas undergoes hydrogen sulfide removal, carbon monoxide shift, carbon dioxide removal, methanation and drying, and final compression. To increase the hydrogen yield, the carbon monoxide and water in the gas are converted to carbon dioxide and hydrogen by the well-known carbon monoxide shift reaction performed with a shift catalyst:

$$CO + H_2O \underset{\text{catalyst}}{\rightleftharpoons} CO_2 + H_2$$

Commercial catalysts for reactions in two temperature ranges (from 350° to 500°F and from 600° to 950°F) are available. The use of a low-temperature shift catalyst requires much less steam than does use of a high-temperature shift system because of the more favorable equilibrium and greater catalyst activity with the former. The lower steam requirement increases the plant thermal efficiency and reduces the boiler cost. However, the low-temperature

shift catalyst cannot be used with gases that contain sulfur. Because the acid gases (hydrogen sulfide and carbon dioxide) must be removed at some stage of the process, it is desirable to remove the hydrogen sulfide prior to, and the carbon dioxide after, the carbon monoxide shift.

In this design, the carbon monoxide concentration is shifted from 59% in the feed to 3% in the effluent. This is less expensive than shifting to an even lower carbon monoxide level and still results in a 93% hydrogen product gas. A total of 53,938 moles of carbon monoxide/hr are shifted in four seven-stage reactors, with a steam-to-dry gas ratio of 0.3 for each stage. The total gas flow is divided into four parallel trains to minimize the pressure drop through the seven stages. Quench water and steam are added between the stages to cool the previous stage effluent to 370°F and to bring the steam-to-dry gas ratio to 0.3. A total of 44,826 moles of steam/hr and 45,104 moles of quench water/hr is required.

Prior to the carbon monoxide shift, hydrogen sulfide is removed in the first stage of a two-stage Rectisol system, which has been successfully demonstrated in commercial operations (e.g., in the Sasol plant of the South African Coal, Oil, and Gas Corp.). The sulfur compounds are removed completely by washing the gas with methanol that has been charged with carbon dioxide at 115°F and 700 psig. The higher operating pressure of the Rectisol system favors the physical absorption of acid gas by methanol. The regeneration of this solvent yields a 25.5% hydrogen sulfide-rich gas that yields 86.1 long tons of sulfur/day in the sulfur-recovery plant, with 250 ppm of sulfur remaining in the gas vented to the atmosphere.

After the carbon monoxide shift, and before going to the second-stage of the Rectisol system for carbon dioxide removal, the effluent is cooled to 115°F by waste-heat recovery and water cooling. The carbon dioxide-rich stream is vented to the atmosphere because it contains less than 5 ppm sulfur.

To achieve a pipeline-gas standard of a maximum of 0.1% carbon monoxide,* the effluent from the second stage of the Rectisol system, which contain 4.8% carbon monoxide, is methanated. A single-stage, recycle-quench methanation

*Because the pipeline gas, which contains toxic carbon monoxide, will eventually be delivered to individual residences, the maximum carbon monoxide level must be this low.

system with a feed temperature of 550°F and an effluent temperature of 900°F is used. The methanation effluent is cooled to 125°F, with a portion of the gas being used as the recycle quench stream. The product gas is dried in a standard glycol drying unit to 7 lb of water/million SCF of gas.

The dried gas is compressed to 1000 psig in a single-stage, product-gas compressor and is sent to the pipeline. Because the heating value of hydrogen is approximately one-third that of methane, per SCF of gas, the volume of the hydrogen product gas is approximately three times that of SNG for a comparable 250 X 10^9 Btu/day plant, or 698 million SCF of hydrogen/day. Table 5-4 shows the composition of the hydrogen product gas.

Table 5-4. COMPOSITION OF THE GAS PRODUCED BY KOPPERS-TOTZEK GASIFICATION
(For a 250 X 10^9 Btu/Day Hydrogen Plant, Operating at 140°F and 1000 psig, That Uses Montana Subbituminous Coal)

	Amount, %
Carbon Monoxide	0.1
Carbon Dioxide*	--
Hydrogen	93.1
Methane	5.5
Nitrogen and Argon	1.3
Total	100.0

* 50 ppm

Table 5-5 shows the process thermal efficiency. Approximately 56.8% of the higher heating value of the feed coal is converted to higher heating value in the product gas, and 0.2% of the feed coal is product sulfur. The other major heat losses are shown in Table 5-6. The remaining 3.3% loss is attributable to waste-heat recovery, the venting of carbon dioxide to the atmosphere, reactor ash, etc.

In summary, production of 250 X 10^9 Btu of hydrogen/day from Montana subbituminous coal, using a Koppers-Totzek gasifier operating at 6 to 7 psig and at 2700° to 3300°F, requires 25,012 tons of 22%-moisture coal per day, thus converting 56.8% of the HHV of the coal to HHV in the product hydrogen.

Table 5-5. KOPPERS-TOTZEK PROCESS EFFICIENCY
(For a 250 X 10^9 Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Amount
Reactor Coal, lb/hr (dry basis)	1,229,590
Boiler Coal, lb/hr (dry basis)	396,218
Total Coal, lb/hr (dry basis)	1,625,808
HHV* of the Total Coal, 10^6 Btu/hr (at 11,290 Btu/lb)	18,355
HHV of the Product Gas, 10^6 Btu/hr	10,429
% Converted to Product Gas	56.8
% Converted to Sulfur	0.2
Total % Converted to Products	57.0

*High heating value.

Table 5-6. HEAT-LOSS SUMMARY FOR THE KOPPERS-TOTZEK PROCESS

	Amounts, 10^6 Btu/hr	% of HHV of Total Coal
Air-Cooling Units	58.3	0.3
Rejected by Cooling Water	6113.2	33.3
Boiler Losses	591.7	3.2
Coal Drying	529.1	2.9
Total	7292.3	39.7

Description of a 250 Billion Btu/Day Plant Producing Hydrogen From Montana Subbituminous Coal by the U-GAS Process

The U-GAS Process utilizes single-stage, fluidized-bed gasifiers. The major advantages of this type of operation include—

- High reaction rates because of good gas-solids contact
- A uniform and easily controlled bed temperature
- A high concentration of carbon in the fluid bed, thus ensuring reducing conditions; giving good product gas; and ensuring that sulfur is converted to hydrogen sulfide, which is readily removed
- An ash-removal system that is unique because it allows for the recycling and subsequent gasification of fines and for removal of only low-carbon ash. This system results in high carbon conversion and, hence, is highly efficient.

Our process designs for hydrogen production are based on the use of Montana subbituminous coal, which is noncaking and thus needs no pretreatment. Coal (22% moisture) is received from the nearby mine at the rate of 21,443 tons/day. For the coal-drying system, 16,760 tons of process coal (22% moisture) per day are required, and the boiler requires 4148 tons of coal (22% moisture) per day. (See Figure 5-3.)

Coal is simultaneously crushed to 1/4-inch x 0 size and dried to a moisture content of 10% before being conveyed to the reactor feed system. Lock hoppers have been chosen for this feed system because they have been commercially proved in systems operating at this reactor pressure (335 psig). Coal is dropped from a feed bin into an open lock hopper. After being isolated by the lock hopper valves, the lock hopper is pressurized (with nitrogen from a recycle nitrogen compressor) to the reactor pressure. The lock hopper discharge valve is then opened; and the contents of the lock hopper flow, by gravity, into a continuous reactor feed bin. The pressure in the lock hopper is then released to a surge drum upstream of the recycle compressor, and the cycle begins again.

Generation of Synthesis Gas

This plant requires two gasifiers, each with an inside diameter of 31 feet and a 68-1/2-foot straight shell. These two units consume 8631 tons of 98% oxygen per day, combined with 375,776 lb of steam/hr. The steam and oxygen serve as a fluidizing-gasifying medium for the 14,525 ton/day gasifier coal feed. Table 5-7 shows the gasifier feed quantities and the steam required for the carbon monoxide shift.

Table 5-7. U-GAS GASIFIER FEED QUANTITIES
(For a 250 X 10^9 Btu/Day Plant That Uses Montana Subbituminous Coal)

	Amount
Coal, lb/hr (dry basis)	1,089,399
Steam, lb/hr	375,776
Oxygen, tons/day	8,631
Steam for the Shift, lb/hr	790,758

The coal is gasified in a single-stage fluidized bed at 1900°F and 335 psig. Reactor residence time is 80 minutes, and the fluidizing velocity is 1.5 ft/s. Because the coal is injected below the surface of the fludidized bed, methane

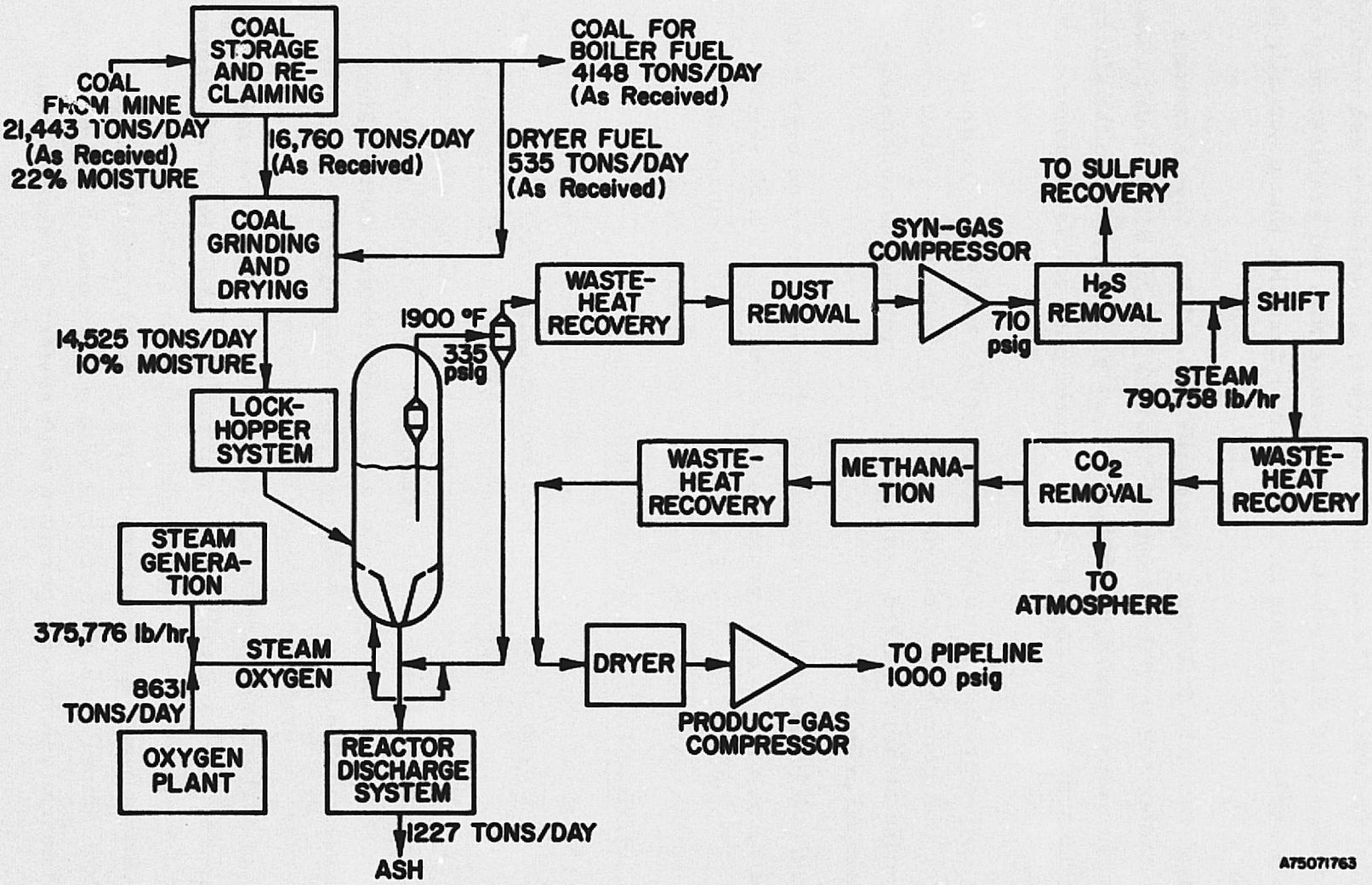


Figure 5-3. U-GAS GASIFIER FOR HYDROGEN

formation is minimized; and, because of the high temperature, devolatilization products are decomposed. The gasifier is unique in its method of ash removal and fines handling. (See Figure 5-4.) Simultaneous with the gasification of the coal, the ash is agglomerated into larger, heavier particles that eventually fall out of the bed.

The ash agglomerates fall into a water-filled quench pot, thus forming a slurry that is cooled and then depressurized across a valve before being channeled to one of two slurry-settling ponds. The water is recycled to the slurry quench pot. The ash is reclaimed from the unused pond and is disposed of in the mining area.

The raw gasifier product is cooled from 1900° to 300°F in a waste-heat recovery boiler that generates about 90% of the required process steam (the remaining process steam required being generated in the carbon monoxide-shift waste-heat recovery unit).

Small dust particles (less than 5 microns in diameter) carried over from the cyclones are removed in a jet venturi scrubber that has a high removal efficiency for particles of from 1 to 2 microns in size. This completely removes particulate matter from the gas before it is compressed.

The Manufacture of Hydrogen From Synthesis Gas

Table 5-8 shows the composition of raw synthesis gas and product gas. To increase the hydrogen yield, the carbon monoxide and water in the gas are converted to carbon dioxide and hydrogen by the well-known shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) performed in a catalytic reactor. Commercial catalysts for reactions in two temperature ranges (from 350° to 500°F and from 600° to 950°F) are available. The use of a low-temperature shift catalyst requires much less steam than does use of a high-temperature shift system because of the more favorable equilibrium with the former. In this case, 45,275 lb-mol of carbon monoxide/hr are being shifted. The low-temperature shift system saves either 1.2 million or 2 million lb of shift steam/hr, depending on whether the system used as a comparison is a) an all-high-temperature shift catalyst with no water quench between stages or b) a combination high temperature-low temperature shift catalyst with a water quench between each stage. Also, because the low-temperature shift system decreases steam

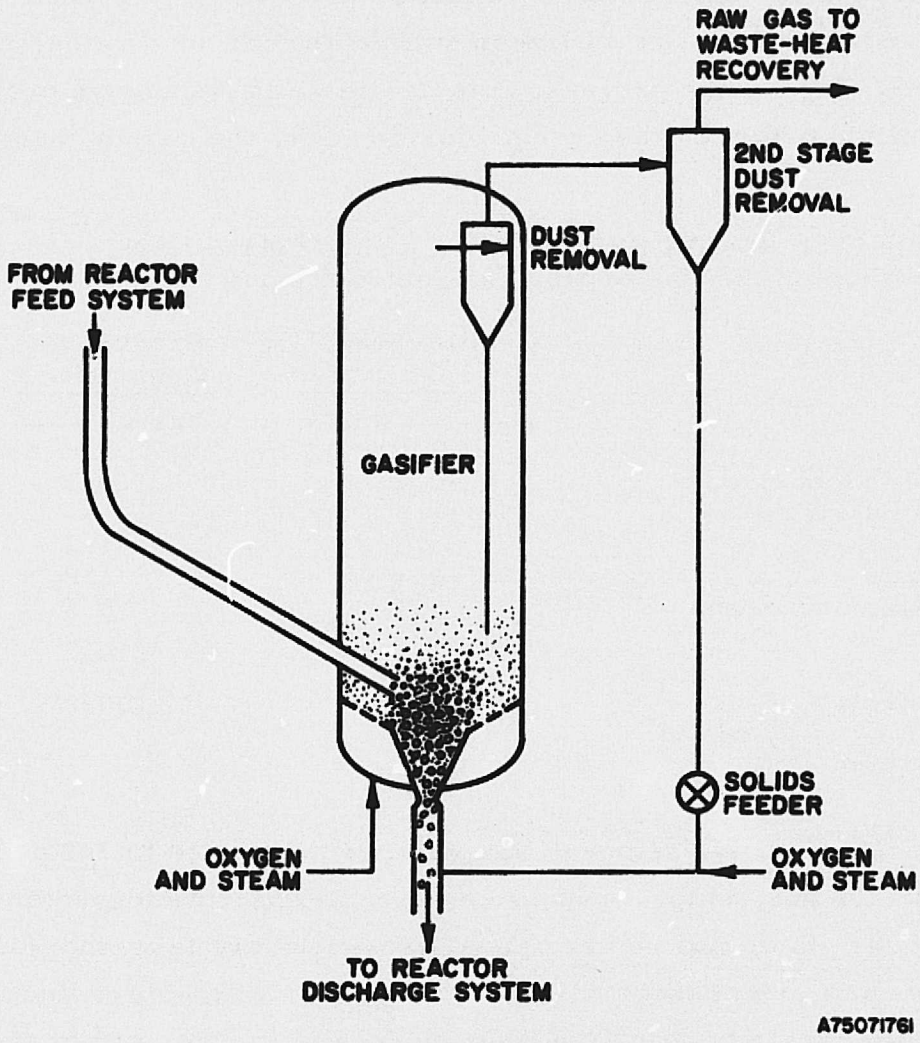


Figure 5-4. SIMPLIFIED DIAGRAM OF THE GASIFIER TO BE USED IN THE IGT U-GAS SYSTEM WHEN PRETREATMENT IS NOT REQUIRED

usage, the cost of the boiler is less; and, more importantly, the plant is more efficient by from 3% to 7%, again depending on the type of high-temperature shift system used as a comparison.

The low-temperature shift catalyst cannot be used with a gas that contains sulfur. Because the acid-gases (hydrogen sulfide and carbon dioxide) must be removed at some stage of the process, it is desirable in our design to remove the hydrogen sulfide prior to, the carbon dioxide after, the carbon monoxide shift.

Table 5-8. U-GAS HYDROGEN-FROM-COAL PLANT
(Based on the Use of Montana Subbituminous Coal)

	Gasifier Raw-Gas Composition	Product-Gas Composition
	mol % (dry basis)	
Carbon Monoxide	50.1	0.1
Carbon Dioxide*	11.5	--
Hydrogen	35.3	94.3
Methane	2.1	4.8
Nitrogen and Argon	0.7	0.8
Hydrogen Sulfide	0.3	--
Total	100.0	100.0

*50.0 ppm

Prior to hydrogen sulfide removal, the gas is compressed to 700 psig. This facilitates acid-gas removal because a physical absorption system has been chosen for the plant, and higher partial pressures are favorable for absorption. The unit selected for acid-gas removal is a two-stage Rectisol plant that is similar to units that have been successful in commercial operations. The hydrogen sulfide absorption system produces hydrogen sulfide-rich gas that yields 76.1 long tons of molten sulfur per day in the sulfur-recovery unit, with 250 ppm of sulfur remaining in the gas vented to the atmosphere.

After shifting, the carbon dioxide is removed in the second stage of the Rectisol unit. This carbon dioxide-rich stream is vented to the atmosphere. (The sulfur content is claimed to be less than 5 ppm.) A methanation unit is used to reduce the carbon monoxide content of the product gas from 1.5% to 0.1%. This is more economical than using the shift reaction to convert all of the carbon monoxide. The unit is a single-stage, adiabatic reactor similar to those used in ammonia plants in removing carbon oxides. Water is removed

from the gas exiting the methanator by a standard glycol drying unit. The dried gas is compressed to 1000 psig by the product-gas compressor and is sent to the pipeline.

In terms of volumes of gas handled, this plant is larger than the standard-sized 250 billion Btu/day SNG plant. This plant produces 705 million SCF of hydrogen/day, whereas an SNG plant produces only about 250 million SCF of hydrogen/day.

The plant capital investment has been estimated in terms of mid-1974 costs, and the hydrogen cost has been calculated by the discounted cash flow (DCF) method used in the Final Report of the Supply-Technical Advisory Task Force, Synthetic Gas-Coal prepared for the Supply-Technical Advisory Committee for the National Gas Survey by the Federal Power Commission. The capital cost breakdown is shown in Table 5-9.

Table 5-9. CAPITAL-COST BREAKDOWN
(Mid-1974 Basis)

	10^6
Process Units	151.1
Utilities and Offsites	158.4
Installed-Plant Cost (Excluding Contingency)	309.5
Contingency at 15%	46.4
Total Bare Cost	355.9
Contractors' Overhead and Profit at 15%	53.4
Total Plant Investment	409.3
Return on Investment During Construction	92.1
Start-Up Costs	20.5
Working Capital	17.9
Total Capital Required	539.8

The largest costs are for the hydrogen sulfide and carbon dioxide removal unit and for the oxygen plant. These two plants together comprise 44% of the installed-plant cost. Based on a 16% DCF rate of return with coal costing $0.30/million Btu, the cost of the product hydrogen is $2.17/million Btu. Figure 5-5 shows the calculated price of hydrogen as a function of the price of coal.

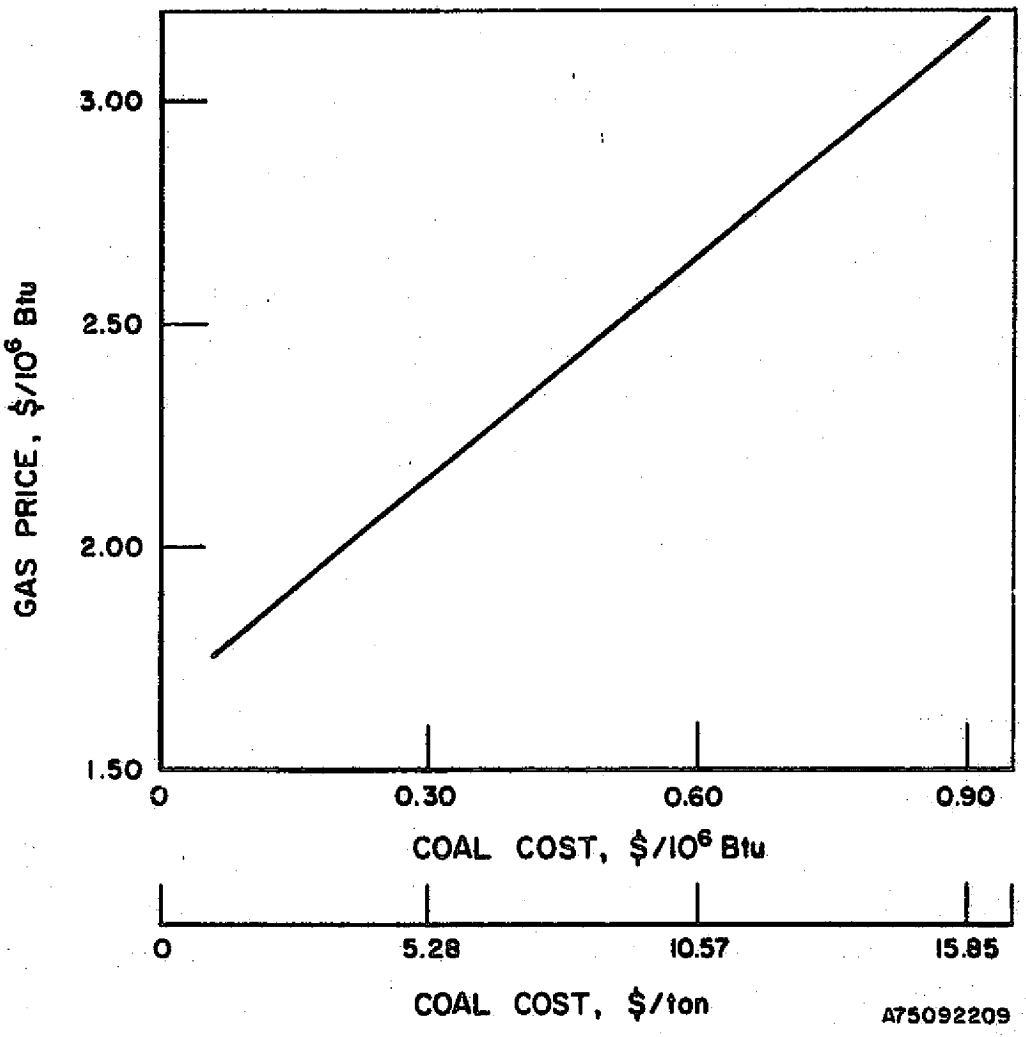


Figure 5-5. GAS PRICE VERSUS COAL COST (250 X 10^9 Btu/Day Hydrogen Plant, U-GAS Gasification of Montana Subbituminous Coal)

The process-efficiency calculation is shown in Table 5-10. About 66.2% of the high heating value (HHV) in the coal is converted to HHV in the product gas. Waste-heat recovery units, which reduce the amount of heat lost to the cooling media, have been used to the maximum extent practicable. The total HHV of the coal used in this process is 15,736 million Btu/hr, of which 1972 million Btu/hr (12.5%) is recovered by waste-heat recovery units. The product gas has a total HHV of 10,425 million Btu/hr (66.2% of the total HHV of the coal). Other major heat losses are shown in Table 5-11.

Table 5-10. U-GAS PROCESS EFFICIENCY

	Amount
Reactor Coal, lb/hr (dry basis, 11,290 Btu/lb)	1,089,399
Boiler Coal and Dryer Fuel, lb/hr (dry basis)	304,363
Total Coal, lb/hr (dry basis)	1,393,762
HHV of the Coal Used, 10^6 Btu/hr	15,736
HHV of the Product Gas, 10^6 Btu/hr	10,425
% Converted to Product Gas	66.2

Table 5-11. SOURCES OF HEAT LOSS IN THE U-GAS PROCESS

	Heat Loss, 10^6 Btu/hr	% of Total HHV of Coal
Air-Cooling Units	898.8	5.7
Rejected by Cooling Tower	3050.9	19.4
Boiler Losses	456.6	2.9

The remaining losses are each less than 2% of the total HHV of the coal consumed and are attributable to such things as the venting of carbon dioxide to the atmosphere, the coal dryer, the combustion-gas vent, by-product sulfur, and reactor ash.

In conclusion, the U-GAS Process, which involves operation of a single-stage, fluidized-bed gasifier at 335 psig and 1900°F, will produce hydrogen from Montana subbituminous coal in an environmentally acceptable manner. The efficiency of conversion of the total coal HHV to product gas HHV is 66.2%. The plant capacity is 250 billion Btu of product gas (94.3% hydrogen) per day and the total capital investment is $528 million.

250 Billion Btu of Hydrogen per Day From Montana Subbituminous Coal by the Steam-Iron Process

In this process, the crushed and dried coal is reacted with steam and air to make producer gas, which is used to reduce the oxidized iron from the steam-iron reactor. Hydrogen is derived from water according to the reactions discussed in a later portion of this report section. The advantages of this process include –

- Production of high-purity hydrogen
- No need for an oxygen plant because air is used directly
- No need for a carbon monoxide shift
- Production of a large amount of by-product electric power.

Any type of coal from bituminous to lignite can be gasified in this process. For the caking coals, pretreatment with air at 700° to 800°F is required to reduce the agglomerating tendency. For this design, Montana subbituminous coal was gasified, so no pretreatment was necessary. The steps required in the conversion of coal to hydrogen by this process are shown in Figure 5-6. These steps may be grouped under the following major headings:

- Coal storage and preparation
- Functions of the producer-gas generator and steam-iron reactor
- Upgrading of the oxidizer effluent to the desired hydrogen product
- Power generation from reductor off-gas using a combined power cycle.

Coal Storage and Preparation

The hydrogen plant is assumed to be located near a coal mine that will provide coal for at least 25 years. Raw coal is brought, by truck, from the mine to a storage area where a 60-day supply is maintained. The plant requires a continuous flow of 31,583 tons of the raw coal (22% moisture) per day from the mine. About 3.2% of the feed coal is used as dryer fuel.

The plant feed is ground so that 80% of the mass is below No. 10 U.S. Sieve Series size (2.00-millimeter opening) and is dried to a moisture content of 5.77% in combination grinder-dryer mills. A lock-hopper feed system, which has been used successfully at 300 to 400 psig in commercial Lurgi

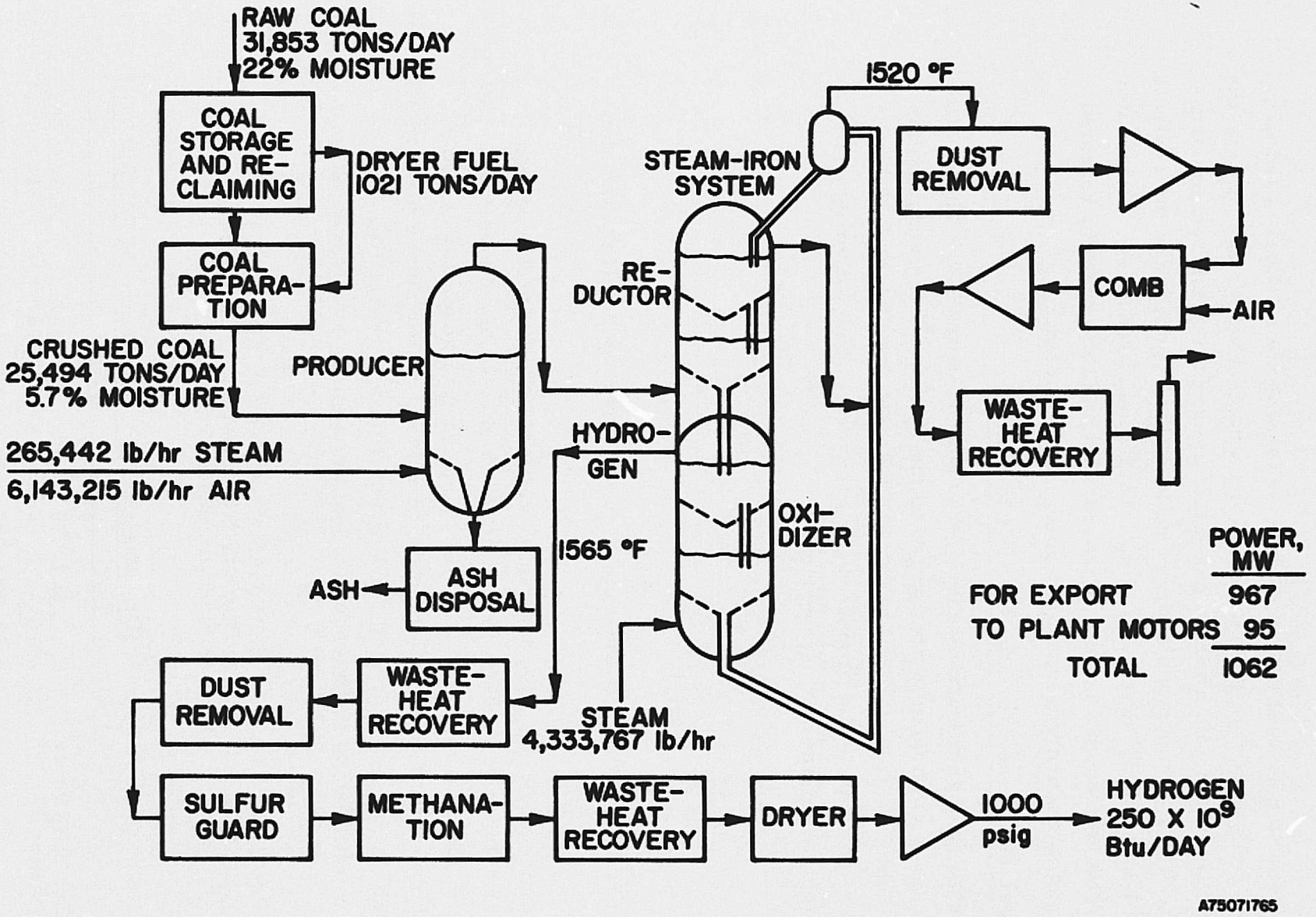


Figure 5-6. STEAM-IRON GASIFICATION FOR HYDROGEN
(For 250 X 10^9 Btu of Product Gas per Day Using Montana Subbituminous Coal)

plants, is used to feed coal to the producer-gas generator. Coal is fed to a lock hopper from a storage bin. After the lock hopper valves are closed, the vessel is pressurized with an inert gas (plant stack gas) to the reactor pressure level. The lock-hopper discharge valve is then opened; and the contents of the lock hopper flow, by gravity, into a continuous producer-gas generator feed bin. The lock hopper is then depressurized, and the cycle is repeated. The inert gas is recovered, recompressed, and recycled.

Producer-Gas Generator and Steam-Iron Reactor

The steam-iron gasification system is shown in Figure 5-7. The ground and dried coal is continuously discharged to the fluidized-bed producer-gas generator, which is operated at 1950°F and 355 psig. A high percentage of the carbon is gasified in the producer-gas generator. The following gasification reactions take place in the producer:

$$C + H_2O \rightarrow CO + H_2 - \text{Heat}$$

$$C + 1/2O_2 + 2N_2 \rightarrow CO + 2N_2 + \text{Heat}$$
(air)

Small quantities of carbon dioxide, methane, and hydrogen sulfide are also formed.

The quantities of coal, steam, and air required for the producer-gas generator are shown in Table 5-12. Table 5-13 shows the composition of the raw producer gas. The residue from the producer-gas generator is cooled to 200°F in a water-filled quench tank. The residue-water slurry is further cooled to 125°F, is depressurized, and is sent to a slurry-settling pond. The water is recycled to the quench pot, and the residue in the pond is disposed of.

Table 5-12. STEAM-IRON GASIFICATION FEED QUANTITIES
(For a 250 Billion Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Coal (Dry Basis)	Steam	Air
	lb/hr		
Producer-Gas Generator	2,004,079	265,442	6,143,215
Steam-Iron Reactor	--	4,333,767	149,572
Total	2,004,079	4,599,209	6,292,787

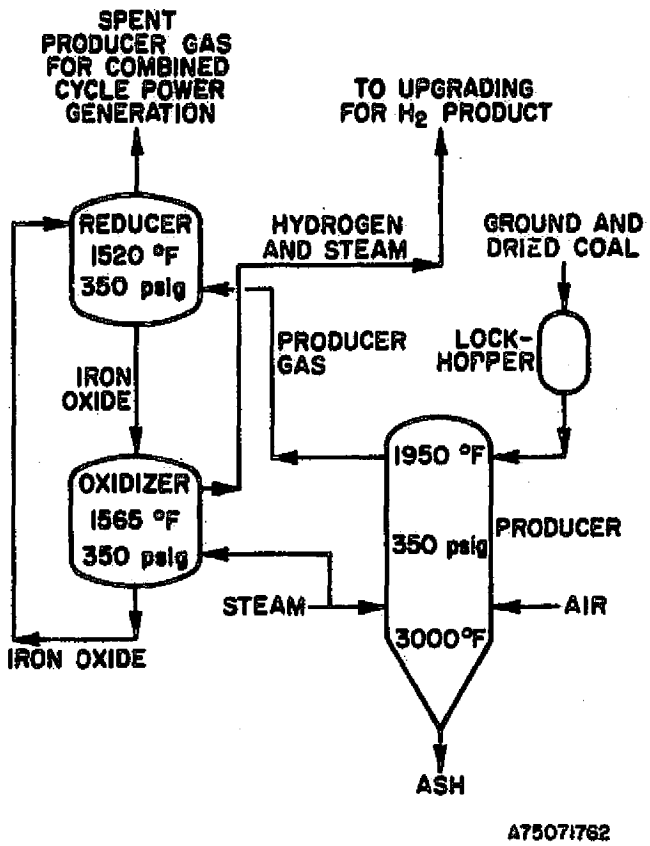


Figure 5-7. STEAM-IRON REACTOR SYSTEM FLOW SCHEME

Table 5-13. STEAM-IRON PRODUCER GAS COMPOSITION
(For a 250 X 10^9 Btu/Day Hydrogen Plant, Operating at 1950°F and 355 psig, That Uses Montana Subbituminous Coal)

	mole %
Carbon Monoxide	27.4
Carbon Dioxide	3.9
Hydrogen	14.3
Water Vapor	4.3
Methane	0.4
Hydrogen Sulfide	0.1
Nitrogen	49.6
Total	100.0

The steam-iron reactor consists of an oxidizer and a reductor. A stream of iron oxide is cyclically reduced with producer gas in the reductor and is reoxidized by decomposition of steam, the hydrogen-forming reactor, in the oxidizer. The following reactions take place in the steam-iron reactor:

Reductor

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$$

Oxidizer

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$

In addition to producer gas, the steam-iron reactor requires additional amounts of steam and air, the quantities of which are shown in Table 5-12. Two effluent streams, one from the oxidizer and one from the reductor, are available for further processing. The compositions of both streams are shown in Table 5-14.

The oxidizer effluent contains primarily hydrogen and steam and is thus upgraded to the desired hydrogen product, whereas the reductor off-gas (spent producer gas) is used for power generation.

Table 5-14. STEAM-IRON REACTOR RAW-GAS COMPOSITIONS
(For a 250 Billion Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Reductor Off Gas (at 1520°F and 350 psig)		Oxidizer Effluent (at 1565°F and 350 psig)	
	Actual	Dry	Actual	Dry
	mole %			
Carbon Monoxide	8.8	10.4	0.5	1.4
Carbon Dioxide	20.7	24.7	0.1	0.2
Hydrogen	6.2	7.4	37.1	95.9
Water Vapor	16.0	--	61.3	--
Methane	0.4	0.5	--	--
Nitrogen and Argon	47.8	56.9	1.0	2.5
Hydrogen Sulfide and Carbonyl Sulfide	0.1	0.1	--	--
Total	100.0	100.0	100.0	100.0

Oxidizer-Effluent Upgrading

The oxidizer effluent contains very small quantities of carbon monoxide and carbon dioxide, but no hydrogen sulfide. This eliminates the need for a carbon monoxide shift and acid-gas removal, so only methanation is required to upgrade the gas to the desired hydrogen product. Because a temperature of 550°F is desirable for the methanation-reactor feed, the effluent is cooled

to 500°F in a waste-heat boiler; and thusly generates about 50% of the steam required for the steam-iron reactor. Before methanation, dust particles are removed by cyclone separators and electrostatic precipitators. The gas passes through a zinc oxide bed as a precautionary step against methanation-catalyst poisoning by any sulfur compound that may have been carried from the reductor to the oxidizer by the iron oxide.

The amounts of carbon monoxide and carbon dioxide methanated are such that the final hydrogen product contains a maximum of 0.1% of both carbon monoxide and carbon dioxide. The methanation reactor is a single-stage adiabatic reactor. The effluent (at 615°F) is used in waste-heat recovery, is cooled to 100°F, is dried in a glycol dryer to 7 pounds of water per million SCF of gas, is compressed to 1000 psig in a product-gas compressor, and is sent to pipeline. The composition of the product gas is given in Table 5-15. The product-gas rate is 768 million SCF/day.

Table 5-15. STEAM-IRON GASIFICATION PRODUCT GAS COMPOSITION
(For a 250 Billion Btu/Day Hydrogen Plant, Operating at 140°F and 1000 psig, That Uses Montana Subbituminous Coal)

	Amount, mol %
Carbon Monoxide	0.1
Carbon Dioxide	0.1
Hydrogen	95.7
Methane	1.5
Nitrogen and Argon	2.6
Total	100.0

Power Generation From Reductor Off-Gas Using a Combined Power Cycle

To extract maximum power, the system incorporates the use of a gas turbine, an expander, compressors, and a steam turbine. The amount of hydrogen sulfide in the reductor off-gas is so low that the pounds of sulfur dioxide per million Btu of total coal to the plant is below the specified limit. Thus, no sulfur-removal system is specified. After the removal of dust by cyclone separators and electrostatic precipitators, the effluent is expanded to 125 psig and 1165°F, recovering power to drive the producer air compressor. The expanded gas is burned with air, in a combustor, at 125 psig and 2400°F. The effluent from the combustor is expanded, in a gas turbine, to

20 psig and 1690°F. A portion of the expansion power is used to drive combustor and producer air compressors that are on the same shaft. The remaining power is converted, in a generator, to 690 MW of electric power. The current maximum temperature range is approximately from 1800° to 2000°F, but gas turbines with an inlet temperature of 2400°F are expected to be available by the time this process is commercialized.

The expanded gas is used in a steam-power cycle to generate 372 MW of electric power from 1200-psig, 900°F steam (generated in a waste-heat boiler) and to generate a portion of the process steam required for the oxidizer. The cooled combustor gas leaves the waste-heat boiler at 350°F. A total of 1062 MW of power is generated, in addition to shaft power used for air compression. Of this amount, 95 MW is used within the plant for motor drives, etc., leaving 967 MW of power as a by-product.

Table 5-16 shows the thermal efficiency of this process. Approximately 44.6% of the higher heating value of the feed coal is converted to higher heating value in the product gas, and 14.1% becomes by-product power (taken at the value of 3413 Btu/kWhr). The other major heat losses are shown in Table 5-17.

Table 5-16. STEAM-IRON-GASIFICATION PROCESS EFFICIENCY
(For a 250 Billion Btu/Day Hydrogen Plant That Uses Montana Subbituminous Coal)

	Amount
Reactor Coal, lb/hr (dry basis)	2,004,079
Boiler and Dryer Coal, lb/hr (dry basis)	66,347
Total Coal, lb/hr (dry basis)	2,070,426
HHV of the Total Coal, 10^6 Btu/hr (at 11,290 Btu/lb)	23,375
HHV of the Product Gas, 10^6 Btu/hr	10,425
% Converted to Product Gas	44.6
By-Product Power, kW	967,000
By-Product Power, 10^6 Btu/hr (at 3413 Btu/kWhr)	3,300
% Converted to By-Product Power	14.1
Total Products, 10^6 Btu/hr	13,725
Total % Converted to Products	58.7

Table 5-17. HEAT-LOSS SUMMARY FOR THE STEAM-IRON PROCESS
(For a 250 Billion Btu/Day Hydrogen Plant That Uses
Montana Subbituminous Coal)

	Amount, 10^6 Btu/hr	% of HHV of Total Coal
Air-Cooling Units	1798.9	7.7
Rejected by Cooling Water	3051.3	13.1
Cooled Combustor Off-Gas	2474.6	10.6
With Producer Char	1204.2	5.2
Dryer Off-Gas	536.6	2.3
Total	9065.6	38.9

The remaining 2.4% loss is attributable to waste-heat recovery and sensible heat losses associated with various plant streams.

In summary, a 250 billion Btu/day hydrogen plant that uses Montana subbituminous coal and the steam-iron gasification process requires 31,853 tons of raw coal (22% moisture) per day. Of the HHV of the coal, 44.6% is converted to HHV in the hydrogen product, and 14.1% becomes by-product power.

6. HYDROGEN PRODUCTION BY THERMOCHEMICAL METHODS — J. C. Sharer and J. B. Pangborn

Introduction

During recent years, an interest has been generated in thermochemical hydrogen production methods.[9,13,17] Thermochemical hydrogen production is a means of splitting water into its elements, hydrogen and oxygen, via a series of chemical reactions. All chemical intermediates are recycled internally within the process so that water is the only raw material and hydrogen and oxygen are the products. This process must be driven by an external heat source, which could be a high-temperature, gas-cooled, nuclear reactor (HTGR) or a solar furnace. The maximum temperature requirements for heat for most proposed cycles lie within a temperature range of 650° to 1100°C, thus eliminating many of the lower temperature heat sources as potential energy donors.

The objective of using a closed-loop series of chemical reactions is established in order to utilize heat directly as the form of energy for hydrogen production and to use only water as a raw material. This approach differs from the major commercial practice of hydrogen production — i.e., steam reforming of natural gas — because a carbon source is not expended and carbon dioxide is not a coproduct. It also differs greatly from the less common commercial practice of producing hydrogen via electrolysis, where the majority of the energy requirements are supplied in the form of work (electricity). Because of practical limitations in the efficiency of converting heat from a primary energy source (e.g., HTGR or solar furnace) to work (electricity), it may be advantageous to utilize the heat directly at, hopefully, higher overall efficiencies. It should, however, be noted that water splitting processes, whether electrolytic or thermochemical, are limited by the second law of thermodynamics to the extent that heat is converted to the "free" chemical energy of hydrogen. This will be shown in more detail later in this section.

The general scheme of thermochemical hydrogen production is depicted in Figure 6-1, which includes a 2-step example — the cycle postulated by Emil Collett and patented in Great Britain in 1924 (probably the first thermochemical cycle for water splitting).[5]

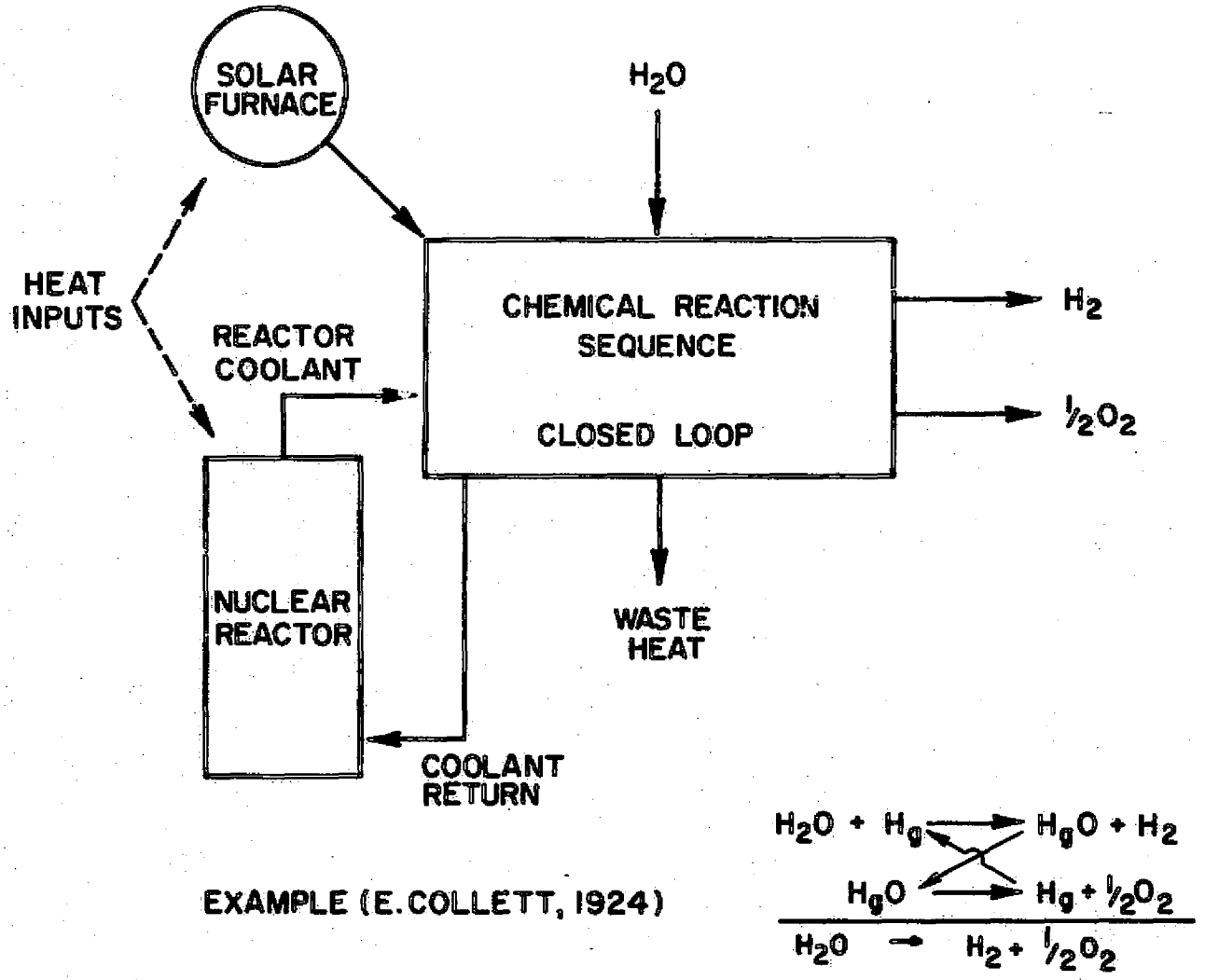


Figure 6-1. THERMOCHEMICAL HYDROGEN PRODUCTION

Water may be chemically decomposed in a single-step reaction. This, however, requires a very high temperature thermal source because temperatures in excess of 2500° C are essential for reasonable reaction yields. Process heat sources are not available at these temperature levels, and the materials requirements for containment and high-temperature gas separations make techniques impractical for large-scale hydrogen production.

Theoretically, a series of two or more chemical reactions can be devised to react water with intermediates, liberate hydrogen and oxygen at different reaction sites, and regenerate all of the consumed intermediates. These (ideal) reactions would be selected so that they could be driven thermally and would not require work. In other words, the free-energy change for each reaction would be equal to or less than zero, and no work would be required for separation of the reaction products. The reaction cycle would be composed of only entropy (heat) requirements. If such a case existed, heat could be used directly, and it would be possible, with the proper choice of reactions, to produce a cycle with very high overall energy efficiency. As will be discussed later, an ideal thermochemical cycle requiring no work does not exist, and there are other considerations that must be examined to determine if a proposed cycle is feasible and practical.

Although thermochemical processes for the production of hydrogen are not in commercial practice today, considerable research is under way at research centers around the world to develop the chemical and engineering technology for thermochemical hydrogen production. Appendix B of this report describes the programs of 23 research groups that deal with thermochemical hydrogen. This information was compiled from the published literature and from private communications (both personal visits and telephone interviews). For each research organization, the appendix includes the organization's address, the duration of its program, a list of nonproprietary cycles, and a list of publications. Because of the proprietary nature of the many programs that are under private sponsorship, full disclosure of the organizations' work is impossible. Therefore, some of the cycles thought to be of high quality in terms of practicality and energy efficiency are not available for publication.

It should also be noted that the development of thermochemical hydrogen production processes is in its infancy stages. Therefore, it is premature to report in detail on process parameters, engineering flowsheets, and cost

analyses of specific processes. Thermochemical hydrogen production on a large-scale basis is probably at least 20 years away. This is indicated by the variety of research organizations doing work in the field and the numerous approaches to this research. For example, an academic institution with governmental funding will have an entirely different approach from an industrially sponsored organization. In addition, an organization with a high level of funding has the opportunity for a more comprehensive program than those groups with programs that can support only one or two researchers. With the many degrees of freedom available in this area of research, almost every organization has a unique approach, with varying goals and abilities to publish or communicate its conclusions. Therefore, compiling and discussing all work done in the area of thermochemical hydrogen production is a difficult task. The information included herein is as complete and accurate as possible as of January 31, 1975.

Table 6-1 presents a summary of the information included in Appendix B. Each research organization is listed with the areas of research that it is involved in. Research activities are divided into seven categories. They are –

- Literature Surveys
- Derivation of Novel Cycles
- Analytical Evaluation of Cycles
- Experimental Evaluation of Cycles
- Comparisons With Electrolytic Hydrogen Production
- Nuclear Reactor Interface Studies
- Detailed Engineering Studies of Chosen Cycles.

Although the level of effort in each activity is not depicted, a notation is established to differentiate between published work, proprietary or unpublished work, and no work for each area.

Basic Thermodynamic Considerations

Because thermochemical hydrogen production schemes are in the early stages of development, a basic thermodynamic approach to prove feasibility is required. The following equation describes the overall system reaction

Table 6-1. AREAS OF RESEARCH ON THERMOCHEMICAL HYDROGEN PRODUCTION BY INTERESTED GROUPS

Group	Research Activities: Literature Surveys	Derivation of Novel Cycles	Analytical Evaluation of Cycles	Experimental Evaluation of Cycles	Comparisons With Electrolytic Hydrogen Production	Nuclear Reactor Interfaced Studies	Detailed Engineering Studies of Chosen Cycles
Aerojet-General Corp., El Monte, Calif.	Reply not received.						
Air Products and Chemicals, Inc. Allentown, Penna.	2	3	3	3	3	3	3
Argonne National Laboratory, Argonne, Ill.	2	1	1	2	3	3	3
Atomic Energy of Canada Ltd., Pinowa, Manitoba	1	3	3	3	3	3	3
Avco Corp., Wilmington, Mass.	Reply not received.						
EURATOM, Ispra, Italy	2	1	1	1	2	1	1
Gaz de France Paris, France	2	2	2	2	2	3	3
General Atomic Co. San Diego, Calif.	2	1	2	2	3	2	2
General Electric Co. Schenectady, N. Y.	2	1	1	2	2	1	1
Holifield Natl. Lab. Oak Ridge, Tenn.	2	2	2	2	3	3	3

Key: 1 = Published Results
2 = Proprietary or Unpublished Work
3 = No Work in This Activity as of January 31, 1975

Table 6-1, Cont. AREAS OF RESEARCH ON THERMOCHEMICAL HYDROGEN PRODUCTION BY INTERESTED GROUPS

Group	Research Activities						
	Literature Surveys	Derivation of Novel Cycles	Analytical Evaluation of Cycles	Experimental Evaluation of Cycles	Comparisons With Electrolytic Hydrogen Production	Nuclear Reactor Interface Studies	Detailed Engineering Studies of Chosen Cycles
Institute of Gas Technology, Chicago, Ill.	2	1	1	2	1	1	3
Iowa State Univ. Amer. Iowa	2	2	2	2	3	3	3
Japanese Govt. (Sunshine Program), Tokyo, Japan	2	2	2	2	2(?)	3(?)	3(?)
KFA (Nuclear Research Center), Jülich, W. Germany	2	2	1	2	3(?)	1	3
KMS Fusion, Inc. Ann Arbor, Mich.	2	2	2(?)	2	3	2	3
Lawrence Livermore Lab., Livermore, Calif.	2	1	2	1	3	3	3
Los Alamos Scientific Lab., Los Alamos, N. M.	2	1	2	2	3	3	3
Pechiney Ugine Kuhlmann, Paris, France	2	3	1(?)	3	3	3	3
Stevens Inst. of Tech. Hoboken, N. J.	1	3	3	3	3	3	3
Univ. of Kentucky Lexington, Ky.	2	2	1	3	3	3	3
Univ. of New Mexico Albuquerque, N. M.	1	3	1	3	3	3	3
Univ. of Puerto Rico Mayaguez, Puerto Rico	2	3	1	3	3	3	3
Westinghouse Electric Corp., Pittsburgh, Penna.	2	2	2	2	2	2	3(?)

Key: 1 = Published Results
2 = Proprietary or Unpublished Work
3 = No Work in This Activity as of January 31, 1975

for all processes producing hydrogen and oxygen from water:

$$H_2O(\ell) \rightarrow H_2(g) + {}_1/_2\ O_2(g) \text{ at } 25°C \qquad (6\text{-}1)$$

If we deal with electrolysis, direct thermal decomposition, or a thermochemical cycle, the net reaction is described by Equation 6-1. For this net reaction, we know that –

$$\Delta H = \Delta G - T\Delta S$$

where –

ΔH = enthalpy change for the reaction

ΔG = Gibbs free-energy change for the reaction

ΔS = entropy change for the reaction

T = temperature of the reaction

A basic proof has been derived that shows that water-splitting processes are subject to a Carnot-type limitation on the transformation of heat into free energy.[8,14] It applies to any water-splitting process in which water is the only raw material and in which the process is driven directly or indirectly by heat. These processes include thermochemical water-splitting cycles, electrolysis (including electricity generation), and direct thermal water splitting. The proof is as follows:

Consider a steady-state process that converts water into hydrogen and oxygen by obtaining heat, q_r, at a constant, elevated temperature, T_r (from a nuclear reactor, for example), and by rejecting heat, q_e, at a lower temperature, T_e, which may be the environment temperature. (See Figure 6-2.) Aside from hydrogen production, the only energy outputs from the process are the heat rejection and the displacement of the environment. The reactant water and product gases enter and exit at the fixed conditions, T_e and P_e.

Writing the first law for such a system, where ΔE is the internal energy change and ΔV is the volume displacement of the environment, Equation 6-2 is obtained:

$$q_e = q_r - Pe\Delta - \Delta E \qquad (6\text{-}2)$$

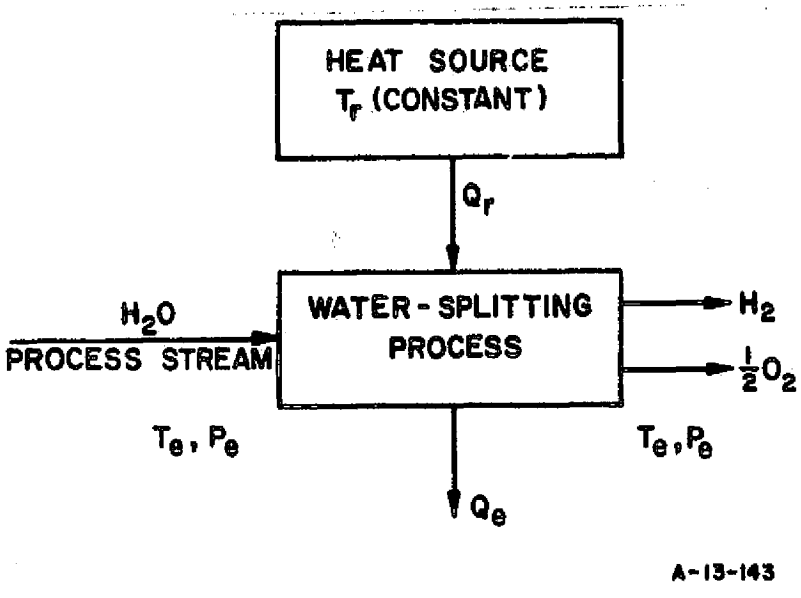


Figure 6-2. IDEAL STEADY-STATE PROCESS TO CONVERT WATER INTO HYDROGEN AND OXYGEN

Denoting the entropy change of the system by ΔS and writing the second law, we derive Equation 6-3:

$$\Delta S \geq \frac{q_r}{T_r} - \frac{q_r}{T_e} \tag{6-3}$$

Combining Equations 6-2 and 6-3 results in Equation 6-4:

$$\Delta E + P_e \Delta V - T_e \Delta S \geq q_r \left(\frac{T_r - T_e}{T_r}\right) \tag{6-4}$$

The corresponding equation for the process stream is —

$$\Delta E + P_e \Delta V - T_e \Delta S = \sum_i \mu_i \Delta n_i \tag{6-5}$$

where μ_i is the chemical potential of a component —

$$\mu_i = \left(\frac{\partial G}{\partial n}\right)_{T,\ P,\ n} \tag{6-6}$$

G denotes Gibbs free energy, and n denotes the number of moles of a component.

Substituting Equation 6-5 into 6-4, Equation 6-7 is obtained:

$$\sum \mu_i \Delta n_i \leq q_r \left(\frac{T_r - T_e}{T_r}\right) \tag{6-7}$$

From the definition of Gibbs free energy and the Gibbs-Duhem Equation, $SdT + VdP - \Sigma n_i d\mu_i = 0$ (where $dP = dT = 0$ because T is constant at T_e and P is constant at P_e), Equation 6-8 is obtained:

$$\Delta G \leq q_r\left(\frac{T_r - T_e}{T_r}\right) \quad \text{or} \quad \frac{\Delta G}{q_r} \leq \left(\frac{T_r - T_e}{T_r}\right) \tag{6-8}$$

From this relationship, an ideal water-splitting efficiency can be written involving the enthalpy, ΔH, or heating value of hydrogen:

$$E = \frac{\Delta H}{q_r} \leq \frac{\Delta H}{\Delta G}\left(\frac{T_r - T_e}{T_r}\right) \tag{6-9}$$

The efficiency of any given process or cycle should be compared with the best attainable, which is given by Equation 6-9. From the process –

$$H_2O(\ell) \rightarrow H_2(g) + {}_1/_2\, O_2(g)$$

at 1 atmosphere and 25° C, where $\Delta H = 68.3$ kcal/g-mol and $\Delta G = 56.7$ kcal/g-mol, we have calculated the ideal water-splitting efficiencies presented in Table 6-2.

Actual thermochemical water-splitting cycles cannot be evaluated by Equation 6-9; they can only be compared with it, and they cannot exceed it. Theoretically, a cycle might be written so that –

1. All the chemical reactions proceed as written, spontaneously, with no work inputs required (only heat inputs).
2. No gas separations need to be done, and no compression work is required.
3. All the heat required by the cycle is fed in at T_r, all the waste heat is rejected at T_e, and there is perfect internal matching of endothermic and exothermic processes.

When all these conditions are fulfilled, Equation 6-9 can be applied. However, no cycles known to us come close to fulfilling all these criteria. If a given cycle satisfies criteria 1 and 2, but not 3, a simple heat (entropy) balance is adequate, but very few cycles even approximate this circumstance.

For an electrolysis process that operates at 25° C, we know that work must be supplied to the reaction and that, ideally, the quantity of work is equal to the Gibbs free-energy change for the reaction, 56.7 kcal/g-mol of hydrogen. There is also an ideal heat requirement that is equal to the entropy term, $T\Delta S$, which for this reaction is equal to 11.6 kcal/g-mol of hydrogen. We do produce hydrogen that has a high heating value equal to the

Table 6-2. IDEAL WATER-SPLITTING EFFICIENCIES

T_r °C	T_e °C	q_r kcal/g-mol	q_e kcal/g-mol	H/q_r	E, %
125	25	222	154	0.307	30.7
225	25	140	72	0.487	48.7
325	25	113	45	0.605	60.5
425	25	99.8	31.5	0.692	69.2
525	25	90.3	22.0	0.757	75.7
725	25	80.7	12.4	0.846	84.6
1225	25	70.8	2.5	0.965	96.5
1725	25	66.6	−1.7*	1.025	100.0*
4025	25	60.9	−7.4*	1.122	100.0*
∞	25	56.7	−11.6*	1.204	100.0*

*Indicates negative heat rejection q_e at T_e (25°C). To have a process efficiency in excess of 100%, this negative q_e would have to be "free heat" input from the environment. An example would be a 25°C, 1 atmosphere reversible electrolyzer operating at 1.23 volts and supplying exactly 56.7 kcal of electrical energy for each mole of water decomposed. With 100% heat-to-work efficiency ($T_r = \infty$, $T_e = 25$°C), this overall process would be "120%" efficient, but it requires a free entropy input of 11.6 kcal/mole of water decomposed.

negative of the enthalpy change of this overall reaction, or −68.3 kcal/g-mol of hydrogen. The work that is required for the reaction in an electrolysis cell is supplied in the form of electricity, the generation of which is subjected to a Carnot limitation by the second law of thermodynamics. Electricity today has a practical generation efficiency usually in the range of from 30% to 40%.

Because work generating cycles are limited in efficiency by maximum operating temperatures (imposed by available heat sources) and by process materials for heat transfer or containment of working fluids, it would be advantageous to use heat directly in a chemical process, thus avoiding many of the mechanical limitations that cause the practical limitations on efficiency in electricity generation. By using heat directly, it is hoped that one step in an energy conversion process would be eliminated. This is the basic reason for trying to devise a thermochemical hydrogen production scheme.

In reality, there will be work requirements for thermochemical cycles. For example, work will be required to drive some reactions to completion, to perform separations of reaction products, for compression work for reactions that operate at elevated pressures, and to maintain mass transfer and sustain pressure drops in the system. These work inputs can and should be minimized to achieve the maximum operating efficiency of a thermochemical cycle, and this can be accomplished by selecting proper operating conditions for the various chemical reactions. The operating temperatures must be selected so that the heat requirements will fall within some feasible temperature envelope that could be supplied by a nuclear reactor or some other heat source (e.g., solar). From the literature, maximum temperatures in the range of from 900° to 1100°C may be attained by an advanced-technology, high-temperature, gas-cooled nuclear reactor (HTGR).[16,18,19] Limits on solar furnaces for this application have not yet been estimated, although, with concentration, 2000°C temperatures have been achieved for other purposes.[3]

Also essential for a thermochemical cycle is that the net overall reaction for the series of reactions selected be described by water-splitting Reaction 5-1 (i.e., that all intermediates be internally recycled within the process). For example, let's examine a cycle proposed by the Institute of Gas Technology and others,[13] as described below:

$$2CrCl_2(s) + 2HCl(g) \rightarrow 2CrCl_3(s) + H_2(g) \quad 25°C \quad \Delta G_{Rx} = -8.5 \quad (6\text{-}10)$$

$$2CrCl_3(s) \rightarrow 2CrCl_2(\ell) + Cl_2(g) \quad 925°C \quad \Delta G_{Rx} = +15.1 \quad (6\text{-}11)$$

$$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 1/2\,O_2(g) \quad 925°C \quad \Delta G_{Rx} = -5.41 \quad (6\text{-}12)$$

$$H_2O \rightarrow H_2 + 1/2\,O_2$$

The net overall reaction "splits" water into hydrogen and oxygen. The temperatures are selected so that the Gibbs free-energy change for each reaction is minimized and so that the temperatures are within an envelope of 25 ° to 925 ° C. Reactions 6-10 and 6-12 have free-energy changes of −8.5 and −5.41, respectively, and theoretically will not require work inputs to generate appreciable quantities of reaction products. Admittedly, this does not include the work inputs necessary for product mixture separation. Reaction 6-11, however, does have a positive free-energy change, +15.1 kcal at 925° C, and will require a work input. We have, however, in theory reduced the work requirements for splitting one mole of water from 56.7 to 15.1 kcal.

This cursory look at the basic thermodynamic considerations for reaction and temperature selection can be summarized as follows. For a promising thermochemical cycle, reactions, and temperatures for those reactions, should be selected so that the free-energy change for each reaction is minimized and should fall within a tolerable range. (Most research organizations have selected a range not larger than −15 kcal to +20 kcal per reaction, per gram-mole of hydrogen produced.) Temperatures should be selected between 25 ° C and some maximum temperature that could be supplied by a futuristic heat source. (This maximum temperature varies between 800° and 1000 ° C, depending on the research organization.)

There are other considerations that must be examined in evaluating thermochemical cycles. Some of these are work requirements for gas separations, the exchange of heat within the cycle, corrosivity of chemical compounds, interfacing the thermochemical cycle with a heat source, and reaction kinetics. These considerations are discussed in the following paragraphs.

Efficiency Calculations for Thermochemical Cycles

Although most research organizations have determined theoretical maximum (ideal) efficiencies for thermochemical cycles, relatively few groups have tried to calculate or estimate realistic values or process operating efficiencies. Each organization has devised its own method of efficiency evaluation that best suits the objectives of its program. To date, no one method has been established as the best approach, although it may be advantageous to determine a scheme that will allow each team of researchers to measure the quality of its cycle against those proposed by others.

Importance of Energy Efficiency for Thermochemical Cycles

The efficiencies of cycles may be the most important criterion in determining the most promising cycle. As in electrolysis, operating costs of thermochemical processes may contribute significantly to the hydrogen production cost. A consideration of the electrolysis process for hydrogen production is useful at this point: For example, Figure 6-3 shows the effect of the cost of electricity on the cost of hydrogen produced by electrolysis.[20]

In Figure 6-3, the abscissa intercepts are directly related to the capital costs for an advanced electrolyzer plant. The slope of the cost lines reflect the electrolyzer efficiency. Because the cost of nuclear electricity is in excess of 10 mills/kWhr, operating costs will be at least 65% to 80% of the production cost of electrolytic hydrogen. The more efficient the electrolyzer operation, the lower the hydrogen cost (after some power cost is assumed).

It is interesting to note that an estimated 67% or more of the proportion of capital costs associated with a nuclear heat supply versus those associated with an entire conventional nuclear-electricity generating plant is attributable to the nuclear heat supply.[11,15] Hence, the nuclear-heat portion of all plant capital costs for electrolytic and thermochemical hydrogen production will be relatively large for processes of reasonable and competitive costs. A recent study[15] that included projections of costs for thermochemical hydrogen placed the nuclear-heat portion of the hydrogen production cost at 44%. Evidently, efficiency of the use of nuclear heat will have a strong influence on both electrolytic and thermochemical hydrogen production – i.e., the greater the efficiency, the cheaper the cost of the hydrogen (for similar plant capital costs).

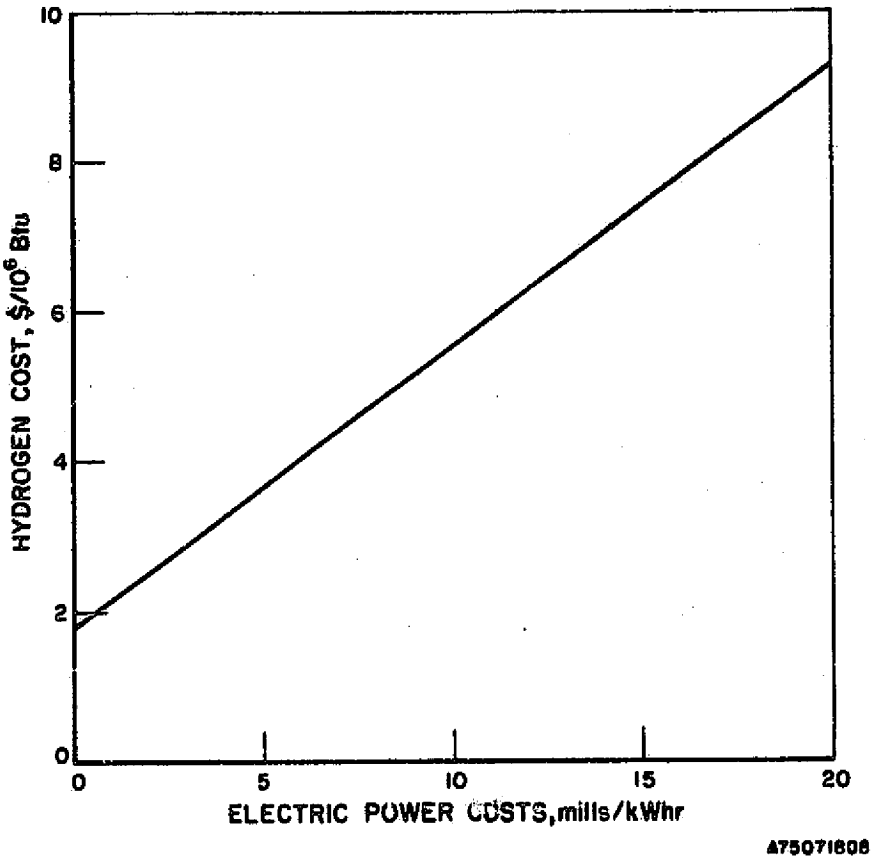


Figure 6-3. COST OF HYDROGEN PRODUCED BY AN ADVANCED ELECTROLYZER

The efficiency of a cycle can be defined as the heat available in the hydrogen produced (usually considered to be the high heating value, HHV, of the hydrogen, or 68.3 kcal/g-mol) divided by the quantity of heat required to produce one gram-mole of hydrogen; this quotient is multiplied by 100.

$$\text{Efficiency} = \frac{\text{HHV}_{H_2}}{\text{Heat Input}} \times 100 \qquad (6\text{-}13)$$

The HHV of hydrogen is recommended as the measure of product energy for three reasons:

1. The HHV is consistent with the overall thermodynamic requirements of water splitting. Liquid water is the primary raw material, and gaseous hydrogen and oxygen are the products. The enthalpy of this decomposition process (at 1 atm and 25° C) is equal to the negative of the HHV of hydrogen.

2. Although most fuel-burning equipment used today does not extract even the low heating value (LHV) of the fuel, energy costs, conservation, and emphasis on efficiency will tend to remedy this waste in the future –

particularly if manufactured hydrogen is the fuel. Laboratory tests of developmental models of hydrogen-burning appliances have already demonstrated that it is possible to extract more than the LHV of hydrogen fuel. Further, it would make little sense to deal with utilization efficiencies exceeding 100% (basis LHV) in the future.

3. The Gas Utility Industry uses the HHV by convention and by statute. This is not arbitrary, but is partly because comparable calorimetry determinations can most easily and accurately be made by condensing the condensable products of combustion (H_2O) and cooling to near room temperature.

Techniques for Estimating Cycle Efficiency

A form of Equation 6-13 is used by almost all research organizations that attempt to estimate cycle efficiencies. However, distinctions between techniques for efficiency estimation (explained below) lie in determining the denominator of the equation. Only a few organizations have not developed efficiency calculation procedures. Usually, these organizations have done valuable survey work and have not been concerned with deriving and evaluating cycles. Examples of such organizations are Atomic Energy of Canada, Ltd., Pechiney Ugine Kuhlmann (Paris), and the Stevens Institute of Technology. Other organizations, such as Lawrence Livermore Laboratory (LLL) and Iowa State University, have been more concerned with cycle chemistry and have not concentrated on efficiency estimates.

The researchers at LLL do, however, employ a simple estimate of "efficiency" in order to measure the quality of one cycle against another. They calculate a heat input that is equal to the sum of the enthalpy changes of all endothermic reactions calculated at 25° C. This is by no means an estimate of process efficiency. Indeed, it is nothing more than a "yardstick" by which to measure the expected energy inputs of cycles.

There are certain reasons for taking this approach. First, it is a quick, simple way to compare cycles. Second, there is extensive thermodynamic data (e.g., enthalpy of formation) for chemical compounds at 25° C, but measured or extrapolated data at higher temperatures is often incomplete. There are also many disadvantages to this simple estimation or comparison procedure. First, it makes no distinction between free-energy (work) requirements and entropy (heat) requirements; and, of course, it does not account for the relative change between the two as a function of temperature for a

chemical reaction. Second, work requirements for reaction product separation are ignored, and these requirements may be significantly different for cycles of "similar" chemistry. Additionally, this procedure does not account for internal heat utilization and rejection (waste) that occurs from heat exchange between steps within the cycle.

Los Alamos Scientific Laboratories (LASL) makes a small addition to the LLL method. Researchers there sum the enthalpy changes of the endothermic reactions calculated at 25° C and add to that the sum of the positive free-energy changes of reactions calculated at 25° C. This total is assumed to be the heat input, and an efficiency is calculated via Equation 6-13.

Again, this efficiency is only used as a measure of quality and should not be confused with process-type efficiencies. However, even as a comparative technique it suffers from some of the deficiencies enumerated above for the LLL procedure. It should be noted that free energy is not equivalent to heat; it generally takes about 3 units of heat to generate one unit of work. Cycles of similar chemistry may require significantly different work inputs, and the LASL procedure partially accounts for this (on a comparative basis) by accounting for reaction free-energy changes — but only at 25° C.

Researchers at Argonne National Laboratories, who have published articles on cycle analysis,[1] have developed a thermodynamic scheme for estimating cycle efficiency or "figure of merit." They prefer to analyze cycles with respect to the operation of a heat engine, and they define a "figure of merit" that is equal to the free-energy change of water splitting at 25° C divided by the heat requirement, as shown in Equation 6-14.

$$\text{Figure of Merit} = \eta = \frac{\Delta G_f^\circ(H_2O)}{2\ (\text{Heat Required})} \qquad (6\text{-}14)$$

To determine the figure of merit for a multistep cycle, a temperature-entropy diagram is constructed. On such a diagram, the reaction steps are isothermal lines at the reaction temperature, and the lines connecting the isotherms represent the heating and cooling of materials streams. A material phase change would also be represented by an isotherm. The enclosed area of the temperature-entropy diagram must be the work accomplished by operating the thermochemical cycle, $\Delta G_f^\circ(H_2O)$. A simplifying assumption is that the heat absorbed and the heat rejected during the heating and cooling of

the reactants and products are equal, so that the reactants are heated to the reaction temperature through perfect heat interchange with the products. The heat required for the cycle is determined mathematically by multiplying the algebraic sum of the entropy changes by the associated temperatures.

The procedure is elegant from the standpoint of thermodynamics; however, it assumes that thermochemical cycles require only heat inputs for operation and that, for comparative analysis, cycles can be evaluated by entropy input only. The idealizations about heat capacity and heat exchange are acknowledged, and the associated errors would be relatively small. However, the work requirements (and the attendant heat energy) to drive reactions, separate products, compress gases, etc., would have to be accounted for separately. These quantities can be large and dissimilar, even for cycles of similar-appearing chemistry.

Researchers at General Electric Co. have published thermochemical cycles and have calculated efficiencies for three of their cycles.[9,10] They calculate the enthalpy changes for reactions at the postulated temperatures and assume that the process heat requirements are equal to the sum of the enthalpy changes for the endothermic reactions. To this value they add between 10% and 15% of that heat as energy needed for pumping and to compensate for miscellaneous losses. (This value was assumed based on similar input requirements of oil refineries.) This total heat requirement is then divided into the low heating value of hydrogen (57.6 kcal/g-mol) to obtain an efficiency. (As previously stated, it is our opinion that the high heating value of hydrogen would be preferable and more consistent.)

The University of Kentucky, EURATOM, and the Institute of Gas Technology have gone a step further with cycle efficiency estimates. They calculate a process heat requirement in the following manner: All heat requirements for endothermic reactions and for heating compounds from one reaction temperature to a higher one are determined. This requires heat-capacity and phase-change data or estimates. Likewise, those process steps in which heat is liberated are determined – that is, those involving exothermic reactions and heat release from cooling a component from some temperature to a lower temperature. Calculations are then performed to determine where, according to temperature levels in the cycle, the available heat can be used to supply endothermic requirements. As much usable heat as possible is

transferred internally between endothermic and exothermic steps. A net heat input is required to satisfy all remaining endothermic reactions and component streams. This is the process heat requirement. (This procedure assumes heat exchange efficiencies of 100%.)

In addition to the process heat requirement, there are work requirements for gas separations, for inputs to drive reactions (mechanical or electrical inputs), and sometimes for compression for elevated-pressure operation. The work term for gas separations is assumed to be equal to the free energy, ΔG, of separation calculated by Equation 6-15:

$$\Delta G_{SEP} = RT\Sigma\, a_i \ln x_i \qquad (6\text{-}15)$$

where –

a_i = moles of gas component i at equilibrium

x_i = mole fraction of gas component i at equilibrium.

Before separation, attainment of either equilibrium concentration at the reaction temperatures or some stated extent of reaction (percent of equilibrium) may be assumed for the mixture of gases.

This manipulation is done for all reactions involving gas separations. When possible and advantageous, IGT uses an additional procedure to cool the gas mixture (to a lower step temperature) before the (mathematical) separation is accounted for. In a case in which work is required to achieve reasonable yields from a chemical reaction, the quantity of work is assumed to be at least the positive free-energy change of the reaction. For example, an electrochemical or electrolysis step is presumed 80% efficient, requiring 125% of the reaction free-energy requirement.

The sum of the work terms is the total work input required for the cycle. At this point, the two research groups manipulate the numbers differently.

The University of Kentucky[7] assumes a heat-to-work efficiency of 30% (constant). They determine the heat required to generate this work, add it to the process heat requirements, assume this to be the total heat input, and calculate an efficiency like Equation 6-13 – or more explicitly, according to Equation 6-16:

$$\text{Efficiency or Figure of Merit} = \frac{HHV_{H_2}}{(\text{Process Heat Input}) + \frac{\text{Work Input}}{0.30}} \times 100 \quad (6\text{-}16)$$

where HHV_{H_2} is the high heating value of hydrogen.

IGT first examines the waste heat from the enthalpy balance – that is, the exothermic heat not available for exchange within the cycle. If heat of a temperature high enough (above 325 °C) to be practically useful in generating work is available, it is converted to work via a power plant with an arbitrarily assumed efficiency. This quantity of work is then subtracted from the cycle work requirement. If more work is required, the heat needed for this work is determined via a power-plant efficiency formula in which the maximum temperature is arbitrarily assumed to be the highest (endothermic) reaction temperature of the cycle and the lowest temperature (for waste heat) is 125 °C. In attempting to calculate a realistic maximum efficiency attainable for a working thermochemical process, IGT uses a limited Carnot factor to determine the work value of heat with respect to temperature. The following equation is used when mathematically converting heat into work:

$$W = \eta Q \left(\frac{T_{MAX} - 400}{T_{MAX}}\right) \quad (6\text{-}17)$$

where –

W = work, kcal

η = fraction efficiency (of Carnot)

Q = heat, kcal

T_{MAX} = maximum temperature of heat from which work can be generated, °K

IGT uses a fractional efficiency, η, equal to 0.5 when calculating efficiencies based on current technology. However, because thermochemical hydrogen production will not be implemented immediately, such work-generating cycles should account for future technological and efficiency advances. Based on projections for an optimized, staged Rankine cycle with mercury topping, IGT uses the values of η according to Table 6-3.

Table 6-3. FRACTIONAL EFFICIENCY OF CARNOT FOR FUTURE-TECHNOLOGY WORK GENERATION CYCLES

Temperature, °K	η
700	0.65
800	0.67
900	0.68
1000	0.69
1100	0.68
1200	0.68
1300	0.67
1400	0.66

To calculate an efficiency, IGT divides the high heating value of hydrogen by the sum of the process heat and the heat required to generate work:

$$\text{Efficiency} = \frac{HHV_{H_2}}{(\text{Process Heat Input}) + \frac{\text{Work Input}}{\eta}} \times 100 \qquad (6\text{-}18)$$

Calculating efficiencies, if done manually, is time-consuming. Therefore, researchers at IGT, the University of Kentucky, and EURATOM (Ispra) have computerized programs for this procedure. (The EURATOM computer program was formulated by the University of Aachen; it is similar to the program at the University of Kentucky.) A computer program makes the task more workable if sufficient property data are available.

Other research organizations have narrowed or isolated their investigations to only a few cycles. Westinghouse Electric Corp., General Atomic Co., and (in some cases) EURATOM have done, or are in the process of doing, engineering flowsheeting. By doing a complete heat and material balance (including pumping and compression requirements) and product separations and recycles and by estimating heat exchanger losses and material makeup, a more exact process efficiency can be generated. This, however, is very time-consuming and costly. In most cases, kinetic data necessary for designing reactors, heat exchangers, and other equipment are not available. Assumptions must be made as to whether steps are heat- or mass-transfer limited. Construction materials or equipment specifications must be decided on; and, though difficult, heat-transfer coefficients must be estimated for the exotic materials and environments. This work is premature for many cycles due to the lack of experimental data. Also, many research organizations have neither the facilities nor a financial budget capable of

handling such work. This type of program necessitates selection of one or two cycles that are assumed to be the most promising.

It should be reiterated that there is a certain Carnot-type limitation for thermochemical cycles. Therefore, other factors being equal, cycles that accept heat at high temperatures should inherently have higher efficiencies than those that accept heat at lower temperatures. For example: A cycle that utilizes heat at 900° C may have a maximum attainable efficiency of 45% and a cycle that operates with a maximum-temperature heat requirement of 750 °C may have a 40% efficiency. In this case (by comparison to a Carnot cycle), the second cycle utilizes the lower quality heat (750 °C and below) more "efficiently" than does the first cycle, even though the first has a 5%-higher overall efficiency. Therefore, energy efficiencies should be normalized with respect to the temperature levels of heat acceptance. The Institute of Gas Technology does this by comparing calculated efficiencies for thermochemical cycles with an ideal efficiency for electrolytic hydrogen production where like quantities of heat are available, at the same temperature as that used within the thermochemical cycle, for generating electricity. Dividing these two efficiencies results in a "water-splitting ratio" that takes into account the quality of the heat utilized.

In summary, there is no accepted standard technique for calculating efficiencies. The term "efficiency" or "figure of merit" is used by all researchers, but the numbers generated by the different groups are not comparable. Even the terms themselves are often misleading. To date, none of the numbers generated could be considered as practical process efficiencies. Rather, they are more correctly construed as maximum attainable efficiencies or figures of merit for various levels of ideality assumed for the cycle in question.

Evaluating Cycles

Thus far, the most generally accepted method of evaluating cycles, energy efficiency, has been discussed. Efficiency (when calculated on a consistent basis) is probably the most important parameter and the best for comparison of different cycles. There are, though, a number of other parameters that should be closely examined when evaluating cycles. The following is a list of the key parameters used by researchers for such evaluations:

- Energy efficiency (figure of merit)
- Heat transfer and reaction rates (kinetics)
- Number of reaction steps
- Corrosive properties of chemical intermediates
- Availability and costs of raw materials (makeup material for the cycle)
- Temperature schedule of heat requirements (heat-source interface).

The extent of consideration of these parameters was determined through personal and phone interviews with a majority of the research organizations listed in Appendix B. Efficient cycles generally have steps that are staged in temperature to accommodate internal heat exchange between exothermic and endothermic steps. Maximizing this internal exchange of heat helps to minimize waste heat. Kinetics have an indirect effect on efficiency, and thermodynamics alone cannot be used to predict the magnitude of this effect. If the kinetics are slow, more heat loss to the environment per unit of hydrogen produced will occur. Rapid kinetics are particularly advantageous for the high-temperature, endothermic steps of a cycle.

One general trend a number of researchers have observed is that the fewer the chemical reactions within the cycle, the higher the predicted efficiency.

This makes sense because there will be fewer heat-transfer steps, fewer gas separations, fewer material-handling steps, and less overall system pressure drop. Hence, the number of chemical process steps is drastically reduced.

Some researchers believe that a 2-step, pure thermochemical cycle can be proved to be thermodynamically impossible when practical temperature conditions are imposed.[1,8] To date, there are no known pure thermochemical cycles — i.e., those that require only heat inputs; and there are no known workable 2-step cycles that are essentially thermochemical.

Some research organizations have presented cycles that are not purely thermochemical; these are termed "hybrids" or "heat-plus-work"[4] cycles. They have one or more reactions that are performed essentially with electrochemical or mechanical work inputs. This scheme is often used when a

reaction within a cycle cannot be thermally driven. For example, if the free-energy change of a reaction is slightly positive, the reaction might be made to proceed if a configuration that allows the imposition of a small electrical potential is feasible. This situation is sometimes observed in mildly endothermic or exothermic liquid-phase reactions in which low-temperature operation is desired. Reactions enhanced by work inputs are characteristically, but not exclusively, those that have increasing free-energy changes with increasing temperature and that have a free-energy change between –5 and +15 kcal at 25° C. A voltage of about 0.3 volts or less theoretically would be required to drive this type of reaction. (The electrolysis of water theoretically requires 1.23 volts.)

The general consensus is that cycles of from 3 to 5 reaction steps look most advantageous from the standpoint of efficiency, practicality, and workability.

Another key parameter considered when evaluating cycles is the corrosivity of the compounds in the cycle. Many of the proposed cycles have compounds that are extremely corrosive to common construction materials, and it is questionable whether there are economically available materials that can contain the compounds and not contaminate them. Therefore, materials that can withstand high temperatures and chemical attack are of utmost importance to thermochemical hydrogen production. Such materials for process equipment for thermochemical cycles have been of moderate concern in a few research programs, notably the EURATOM program. In general, detailed studies of this type are probably premature in view of the state of cycle selection. Corrosivity seems a characteristic of workable cycles; but efforts to develop cycles involving less corrosive, but sufficiently reactive intermediates might be rewarding. A large number of different compounds in a cycle complicates the problem of materials compatibility.

Cycles involving relatively noncorrosive materials are of great interest and are a prime objective of many research programs. One of the problems with thermochemical hydrogen production is that a low-temperature reaction step is often required to close a cycle. Although high-temperature steps usually proceed readily (with good kinetics), the compounds in the cycle must also be sufficiently reactive (corrosive) to proceed at low temperatures. One potential way to decrease corrosivity and still have a workable

cycle is by employing a low-temperature electrolytic step – i.e., by using a hybrid cycle.

During our telephone survey, discussions sometimes arose concerning the availability of compounds that appear as chemical species in many cycles. There are usually two questions regarding them. First, is there enough material available to supply numerous plants with initial raw-material and makeup requirements? Secondly, will the cost of the raw-material charge be prohibitive?

These questions are difficult to answer. It is difficult to estimate the quantity of material necessary to initially charge the process because reaction kinetics are unknown. The faster the cycle kinetics, the higher the hydrogen production rate, or the lower the required materials inventory for a given hydrogen production rate. The makeup requirements are likewise unknown. Again, it should be remembered that the process should be totally contained so that the makeup of intermediate compounds is minimal. Even the smallest "leak" will cause large makeup requirements that could prove too costly for continued economical plant operation.[12]

What will the new demand for some of the less plentiful compounds do to their market prices? It is easy to see the advantages of low cost, plentiful materials, but limiting the number of elements that can be used in thermochemical cycles also limits the number of potential cycles. This question also remains unanswered, but it is agreed that these parameters are of importance when evaluating cycles.

The temperature of the heat required from a heat source is another key parameter that should be considered when evaluating a cycle. An HTGR, for example, might, in the future, deliver helium from its nuclear core at about 1000° C and require that the helium stream be reduced to perhaps 500 °C or below before reinjection to the core. On the other hand, a thermochemical cycle may require a considerable portion of its heat above an isothermal condition for a reaction at, say, 800 °C. Therefore, there must be modifications to the process or a bottoming energy-conversion cycle included so that the heat available from the nuclear reactor matches the load of the combined processes. There are alternatives for thermochemical cycles with problems in this area. First is a need for some electric power to operate pumps, compressors, and other utilities for the process. An

electric generating plant could be the bottoming cycle, utilizing, per the example, the unused portion of the 500° to 800° C heat. Second is the possibility of "stacking" thermochemical cycles, but this may involve difficult process control and heat balancing. This possibility will generally have drawbacks such as extremely complex plant operations and a diversity of chemical process equipment.

To utilize heat from a nuclear source, a compatible thermochemical cycle must accept the heat from the nuclear coolant stream so that the temperature of the stream is reduced to acceptable core reinjection levels.

Summarized here are the attributes of a "good" thermochemical cycle for hydrogen production as derived from the criteria used by the research organizations surveyed in this study:

- A cycle should have a higher efficiency, or at least a more practically attained efficiency, than a proposed electrolysis process using the same temperature energy source.
- The cycle kinetics should not be strongly limited by slow heat-transfer or reaction rates. Fast rates are generally desirable.
- The cycle should have as few reaction and heat-exchange steps, gas separations, and material-transport steps as possible.
- It is desirable that chemical intermediates within the cycle be noncorrosive to construction materials commonly used in the chemical process industry and that exotic construction materials not be required.
- It would be advantageous to use several chemical intermediates that are abundant and inexpensive. A cycle that involves a rare or expensive element is generally undesirable.
- If a thermochemical cycle is driven by heat from a nuclear source, the heat demand should match the heat available from the nuclear coolant stream as it cools. (The inherent isothermal aspect of thermochemical cycles appears to make them adaptable to high-temperature solar applications.)

These criteria are of value when comparing one cycle with another or with the electrolytic splitting of water. Eliminating a cycle because it violates a criterion is not good practice, but selecting one cycle as more promising than another, based on all criteria, is a practical and necessary approach.

Heat Source Specifications and Availability

We have outlined the chemical and thermodynamic bases for thermochemical hydrogen production. Cycles that work in the laboratory and that have promising efficiencies and/or that meet other evaluation criteria are extremely important. At this juncture, however, the future of thermochemical hydrogen production is largely dependent on the development of high-temperature thermal sources. We have shown that, because of the second-law limitation on the splitting of water into hydrogen and oxygen through the application of heat, the highest temperature at which heat can be used may produce the most efficient cycle. By having the largest temperature envelope for selection of reaction operating temperatures, we allow the greatest latitude in chemical-species selection. The question that really should be addressed is: In the foreseeable future, what thermal sources will be available and what temperatures will they attain?

In the last two decades, considerable work has been done in the area of nuclear-reactor development for electric power generation. Recently, however, modest investigations have been directed toward the possibility of using nuclear reactors as sources of process heat. Table 6-4 presents coolant temperature ranges for various types of nuclear reactors that are in operation or are under development.[16]

Most research organizations have chosen a temperature envelope that ranges from a minimum of 25°C to a maximum of between 600° and 1000°C. With this information, from examination of Table 4, and by allowing a 50° to 100°C temperature drop for the heat exchanger between the reactor coolant stream and the high-temperature, endothermic step of the cycle, it is clear that HTGR's will be desired for thermochemical hydrogen production. GCFBR's would be marginal in temperature capability. Other reactor types would serve as well, or better, for electrolysis.

If a hydrogen-energy system is contemplated for the future and if nuclear water splitting is the hydrogen source, then we must plan reactor development to match the production method. At this time, BWR's, PWR's, LTGR's, and even LMFBR's do not appear to be particularly useful for thermochemical hydrogen production. It is disturbing to note that the U.S. breeder reactor program, the success of which is vital for the provision of enough nuclear energy to meet our post-1990 demands, is based upon the

Table 6-4. NUCLEAR REACTOR COOLANT TEMPERATURES

Reactor Type	Coolant	Reactor Core Coolant Exit Temp., °C
BWR (boiling-water reactor, 1957 technology, Vallecitos)	Water	250-325
PWR (pressurized-water reactors, 1957 technology, Shippingport, submarines)	Water	275-350
LTGR (low-temperature, gas-cooled reactor; 1963 technology, Windscale, Great Britain)	Carbon dioxide	350-575
BWR/SH (boiling-water reactor with superheat, current technology)	Water	450-575
LMFBR (liquid-metal, fast-breeder reactor; experimental)	Liquid sodium	450-625
GCFBR (gas-cooled, fast-breeder reactor; experimental)	Helium	500-700
HTGR (high-temperature, gas-cooled reactor; 1967 technology, Peach Bottom)	Helium	780-900
HTGR-Otto (same as above with "Otto" fueling scheme, experimental, Germany)	Helium	900-1000
UHTGR (same as above, 1969 experiments, LASL)	Helium	1000-1300
Rover (nuclear rocket power plant, 1970 to 1972, LASL or Aerojet-Westinghouse NERVA project)	Hydrogen	2000-2500

LMFBR, which is probably not acceptable as a heat source for a thermochemical hydrogen process.

The nuclear-electric industry has made various estimates of the demands for nuclear-electricity generation capacity through the years 1990 and 2000. We have considered, for the purposes of illustration, the extra amount of nuclear capacity that will have to be developed to meet the deficit in natural gas supplies that are projected to exist in the year 2000. Estimates of the demand for natural gas in the year 2000 are on the order of 65 trillion SCF/yr, and it is generally accepted that only about half of this demand will be met with domestic, imported, and substitute natural gas sources. Thus, a deficit of about 33 trillion SCF/yr (or 33 quadrillion Btu/yr) is expected.

This deficit can be compensated for in three ways. One way is to altogether deprive the U.S. energy market of this energy, requiring enormous conservation measures and probably resulting in a lowering of economic standards throughout the country. Another way is to meet this energy demand with nuclear-generated electricity, thus requiring major installations of new transmission, distribution, and utilization equipment. The third way is to supply synthetic hydrogen, made through use of a nuclear energy source to a part of the U.S. gas market. The nuclear capacity that would then be required is within the currently anticipated capability of the nuclear industry.

Assuming that reactor materials technology allows for HTGR process-heat production at 925 ^{o} to 1000 ^{o}C in the time frame with which we are concerned, we can reasonably anticipate a practical thermochemical hydrogen production efficiency of about 50%. To produce 33 quadrillion Btu/yr of hydrogen (to meet the gas deficit for the year 2000), we will need a nuclear plant capacity of 66 quadrillion Btu/yr, or 2250 GW (thermal). Because nuclear plant capacities today are conventionally expressed in electrical generating units, it is convenient for purposes of comparison to correct 2250 GW (thermal) to an equivalent 700 GW (electric), assuming a typical 31% nuclear generating efficiency (40%, or 900 GW, for all new-technology HTGR's).

Can an extra 700 GW (electric) of nuclear generation be provided by the nuclear industry? Allowing a 20% downtime for maintenance, refueling,

etc., we are really asking for about 850 GW (electric) of plant capacity. Figure 6-4 shows two projections by the Atomic Energy Commission (AEC)[21] and one by the Atomic Industrial Forum (AIF)[2] of the growth of nuclear-electric capacity. The lower two lines are the "most likely" case and the "high" projected case by the AEC. The top line is the AIF's indication[9] that a growth rate somewhat greater than the AEC's "high" projection can be maintained by the nuclear industry if necessary. Much of the need behind the AEC's accelerated case is due to an anticipation of a take-over of part of today's fossil-fuel markets by nuclear electricity. It seems reasonable to assume that if, for the sake of this example, nuclear hydrogen is to fill the natural gas deficit, the electric demand will be amply satisfied by the "most likely" case, 1200 GW (electric).

In Figure 6-5, we have superimposed a demand point that corresponds to meeting both the 1200-GW (electric), nuclear-electric demand and the 850-GW (electric) needed to meet the gas deficit projected for the year 2000. In terms of nuclear capacity, we assume that the capability for thermal capacity would be the same, per the AEC and AIF projections, whether the "additional" 2250-GW (thermal) be a mix of reactor types or predominantly HTGR's. Of course, for thermochemical hydrogen production the crucial question is whether or not this projected capability can include a significant HTGR contribution.

It can be seen from Figure 6-5 that achievement of this total nuclear generating capacity is probably within the AIF's projected nuclear-industry capability. However, it is important to realize that this point can only be achieved by the year 2000 if the nuclear industry begins its accelerated growth pattern very soon – say by 1980 – and cannot be met if such a decision to expand is delayed until say, 1995. Thus, an early commitment to nuclear thermochemical hydrogen production seems mandatory if we are to develop the necessary quantity of the type of reactors needed to meet our demands of 25 years hence.

To date, no experimental work has been done on applying solar furnace technology to thermochemical hydrogen production. There are, today, solar furnaces that can attain temperatures above 1000° C.[6] They have the apparent advantage of being able to supply heat at somewhat more isothermal conditions than do nuclear reactors. There are, however, problems with

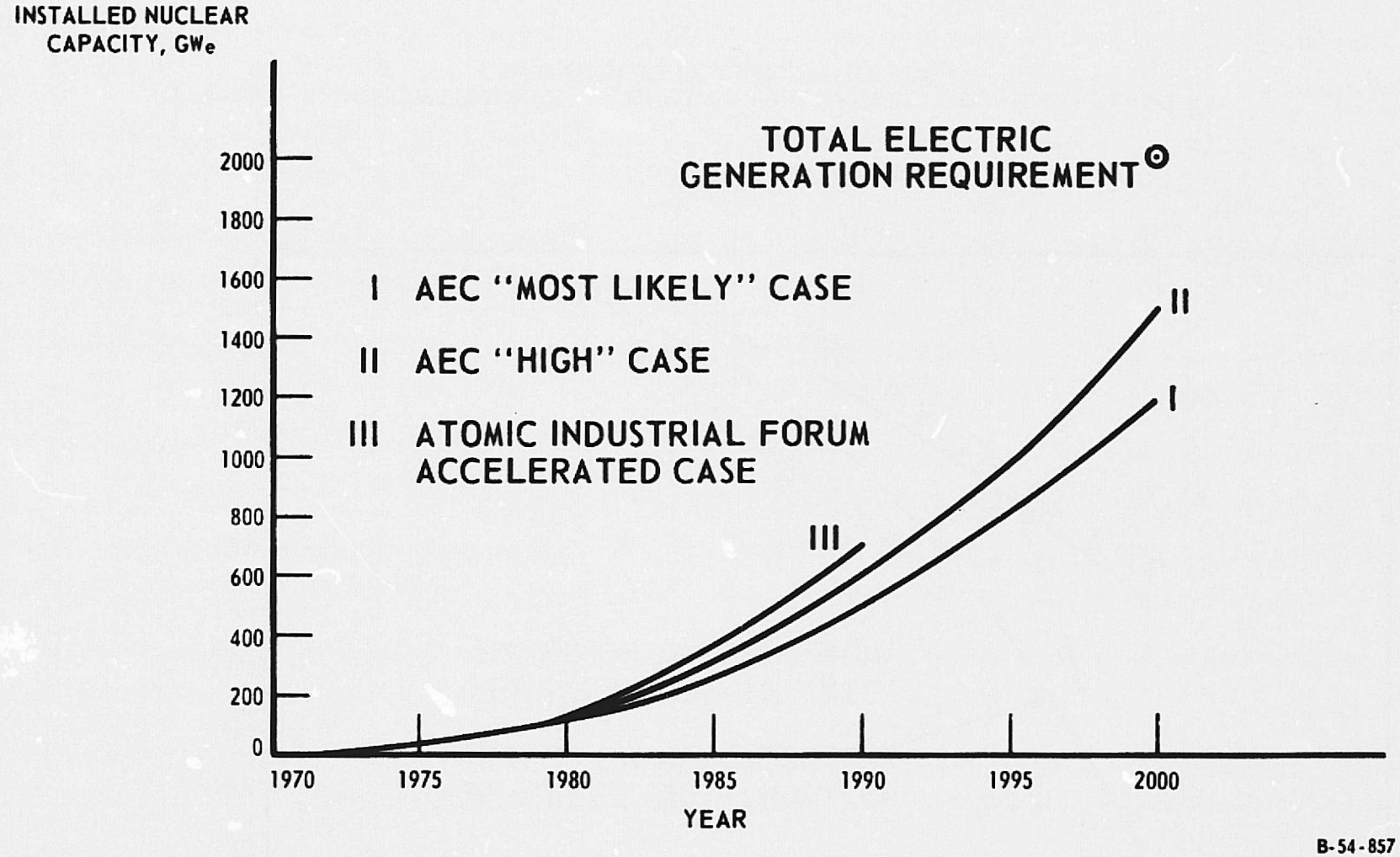


Figure 6-4. PROJECTED GROWTH OF U.S. NUCLEAR CAPACITY
(Source: AEC WASH-1139 and Atomic Industrial Forum)

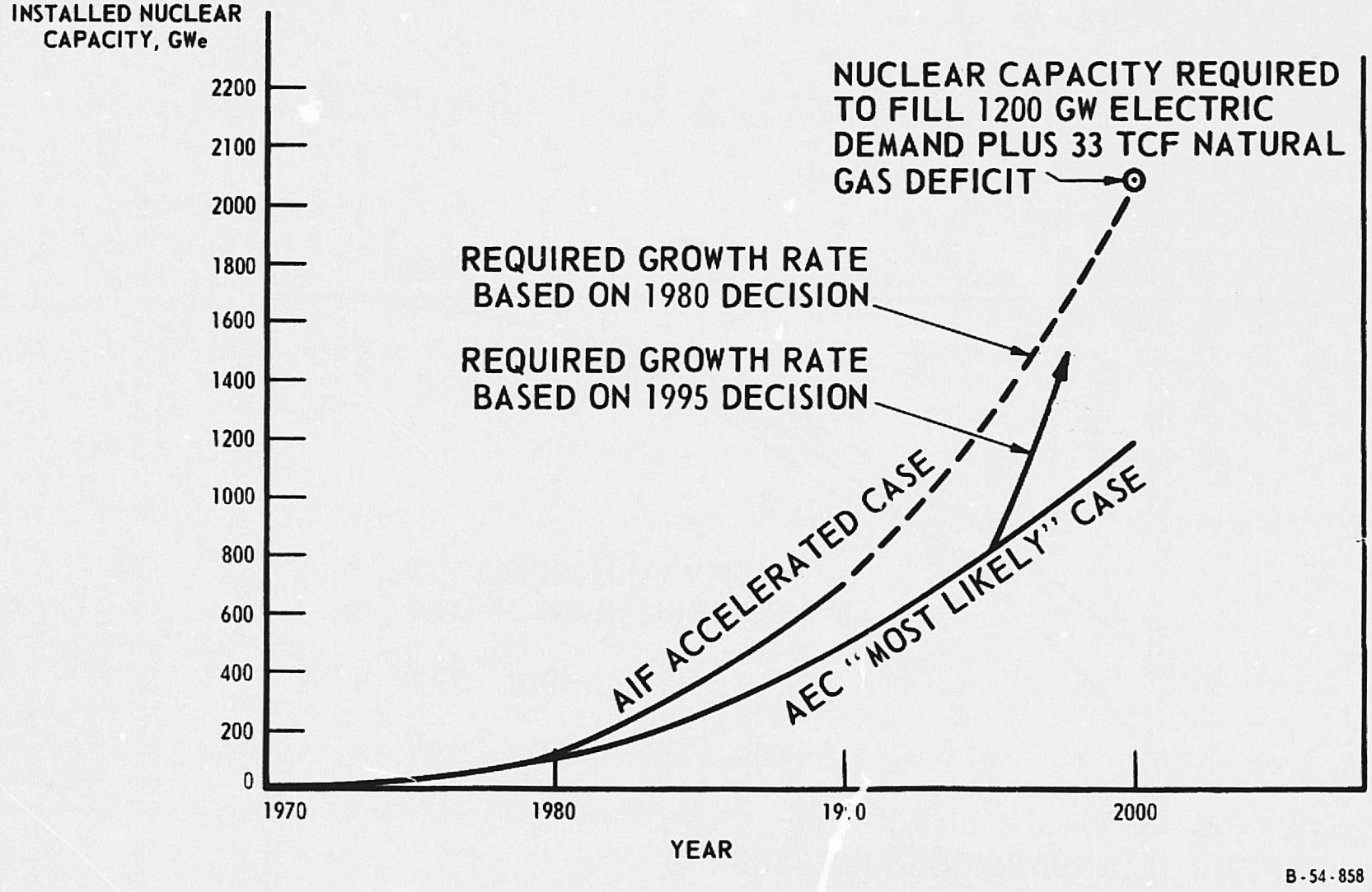


Figure 6-5. GROWTH RATE OF NUCLEAR CAPACITY REQUIRED TO MEET GAS AND ELECTRICITY NEEDS

transient operating conditions for chemical process equipment and/or difficulties in high temperature heat storage during overcast periods and nighttime. These problems might be overcome by use of relatively uncomplicated, high-temperature thermochemical cycles of not more than 3 reaction steps that could be operated efficiently and intermittently.

Technology Development and Identifiable Gaps

The development of technology for thermochemical hydrogen production, as an approximate consensus constructed after our interviews, is depicted in Figure 6-6. The series of stages is intended to portray an orderly development of the technology. The series was developed after interviews with over 20 groups recently and/or currently involved in research on thermochemical hydrogen production. On the average, the state of technology for the various programs surveyed is at stage 3 or 4. A few groups are still working at stage 1. A few others have progressed to stage 8; but this rapid progression has not included most of stages 4 and 6, and it has not included any of stage 7. (Depending on its facilities and philosophy, it may be expeditious for an organization to delay stage 7 until stage 8 is completed.) Most of the research groups interviewed placed attainment of stage 10 in 1985 or later; and most groups at stage 3 or 4 placed attainment of stage 7 in from 1978 to 1980 with annual funding requirements of from $500,000 to $1 million and on condition that, at this point, one cycle be selected for further development.

It should also be stressed that it is difficult to determine the state-of-the-art for thermochemical hydrogen production. Every research organization has a unique approach with independent objectives and direction. Many organizations have taken a proprietary stand, and their "best" work is unavailable. Some research that is sponsored by private industry is protected from public disclosure at this time.

The overall objective of several research programs is, however, demonstration of a cycle in the laboratory. It is hoped that within five years, a bench-scale demonstration will be in continuous or semicontinuous operation. Researchers at some organizations, such as at LASL, IGT, GE, EURATOM, and LLL, have proved the feasibility of individual reactions. Some (those at LASL, IGT, and EURATOM) have demonstrated cycles by recycling materials through each reaction step in a batch-type operation;

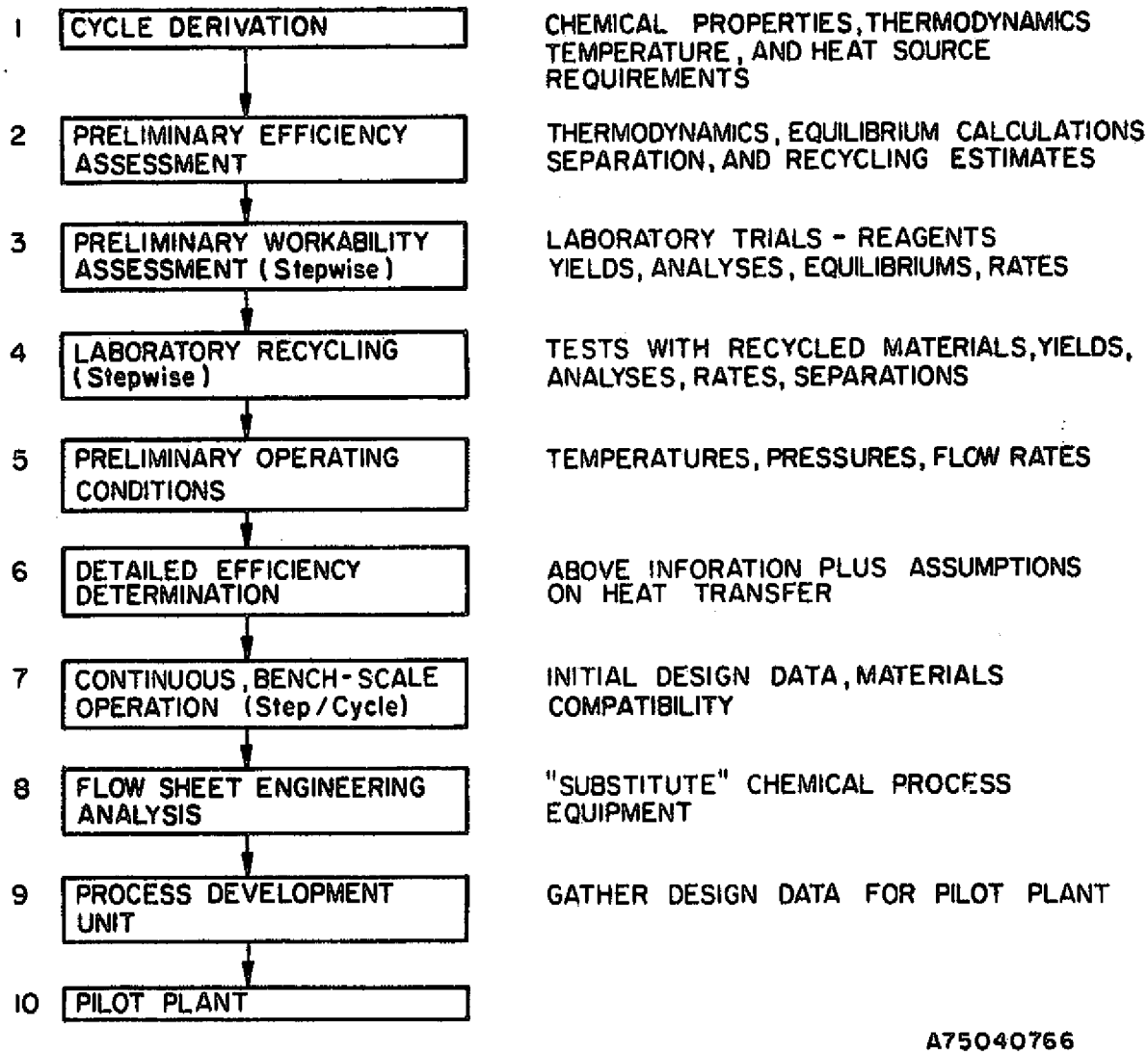


Figure 6-6. REQUIREMENTS FOR TECHNOLOGY DEVELOPMENT IN THERMOCHEMICAL HYDROGEN PRODUCTION

but to date, none has set up a continuously operative cycle in the laboratory. To do this, a research group must first select one cycle. At this stage, it may be difficult for most groups to make such a selection with any degree of confidence. If this were done, it would imply that the organization either believed that this cycle would prove to be one of the best or that they had sufficient funding to allow them to make additional searches for better cycles in parallel efforts.

To build a continuous bench-scale operation, kinetic data on all reactions are required so that reactor design and sizing will allow compatible and balanced material flows throughout the demonstration system.

The objective of other programs is to eventually do engineering designs of proved cycles. These could be used to generate flowsheet-based costs for thermochemical hydrogen production — something that has not yet been achieved; but, for at least one program, will soon be. When asked about capital and operating cost requirements for thermochemical processes, most organizations would not comment; and none had "hard data" to present. Considerable work will be required to generate the cost figures, but the eventual implementation of thermochemical hydrogen will depend on economics.

One important factor brought out by ongoing research is that currently identified technology gaps would limit the practicality of thermochemical hydrogen production. The areas in which research is required can be isolated, and appropriate research programs can be initiated now to find solutions before the world's energy demands include large-scale utilization of hydrogen fuel.

One main area that requires further development is the high-temperature heat exchanger for transferring heat from the nuclear reactor to the endothermic steps of the thermochemical process. Because highly efficient utilization of heat is of utmost importance, heat exchangers will play a prime role in thermochemical plant designs. High surface area, high-efficiency heat exchangers must be developed that will withstand 800° to 1000° C temperatures, with ultrapure helium on one side and, possibly, corrosive atmospheres on the other side. They must be of reasonable size, cost, and expected lifetime.

The availability of materials that can handle the chemical environments is an area that will require extensive testing and development work. Needs

for materials for particular functions in thermochemical cycles have not yet been extensively identified. Before commercialization, some of the cycles will require new materials to ensure adequate life for reactor vessels and piping exposed to corrosive atmospheres at high temperatures. Construction materials are evidently a limiting factor in determining the practicality of many of the proposed cycles.

As discussed previously, high temperature heat sources are currently under development. In Germany (KFA) and in Japan, extensive work is under way on the development of HTGR's with coolant stream temperatures in excess of 950°C. Because efficient thermochemical hydrogen production methods require such temperatures, the future of these methods is dependent on the successful completion of this work. The possibility of other high-temperature sources, such as solar furnaces, has not been fully explored.

One other area of concern with nuclear reactors involves the containment of helium in the coolant loop. It has been observed that in some test loops, operating in temperature ranges of 500° to 1000°C, a complete recharge of helium is required each year. With increased usage of HTGR's, this practice could become cost- or supply-limited.

Work on solutions to the problems anticipated in connection with the gaps in hydrogen production technology should be incorporated into an overall program of hydrogen research. The future of thermochemical hydrogen production is dependent on finding these answers; the merits of the hydrogen production method are clear and warrant such investigations.

References Cited in This Section

1. Abraham, B. M. and Schreiner, F., "General Principles Underlying Chemical Cycles Which Thermally Decompose Water Into the Elements," Ind. Eng. Chem. Fundam. 13, 305-10 (1974).

2. Atomic Industrial Forum, Resource Needs for Nuclear Power Growth, New York, 1973.

3. Bilgen, E., "On the Feasibility of Direct Dissociation of Water Using Solar Energy." Paper presented at the Hydrogen Energy Fundamentals Symposium, Miami, March 3-5, 1975.

4. Bowman, M. G., "Fundamental Aspects of Systems for the Thermochemical Production of Hydrogen From Water." Paper presented at the First National Topical Meeting on Nuclear Process Heat Applications, Los Alamos, N.M., October 1974.

5. Collett, E. (assigned to Synthetic Ammonia and Nitrates Ltd.), "Improved Process for the Production of Hydrogen," Br. Patent 232,431 (1924) May 28.

6. Daniels, F. and Duffie, J., Eds., Solar Energy Research, 155-71. Madison: University of Wisconsin Press, 1961.

7. Funk, J. E., "Evaluation of Multi-Step Thermochemical Processes for the Production of Hydrogen From Water." Paper presented at the THEME Conference, Miami, March 1974.

8. Funk, J. E. and Reinstrom, R. M., "Energy Requirements in the Production of Hydrogen From Water," Ind. Eng. Chem. Process Des. Dev. 5, 336-42 (1966) July.

9. "G.E. Process Could Make Cheaper H_2," Chem. Eng. News 46, (1968) November 4.

10. Hanneman, R. E., Vakil, H. and Wentorf, R.H., Jr., "Closed Loop Chemical Systems for Energy Transmission, Conversion, and Storage." Paper presented at the Ninth I.E.C.E.C., San Francisco, August 1974.

11. Jacobson, N. H., "Problems Abound but So Does Optimism," Combustion 44, 6-9 (1973) June.

12. Joly, F., "Economic Criteria of Selection for Closed Cycle Thermochemical Water Splitting Processes." Paper presented at the T.H.E.M.E. Conference, Miami, March 1974.

13. Marchetti, C., "Hydrogen and Energy," Chem. Econ. Eng. Rev. 5, 7-25 (1973) January.

14. Pangborn, J. B. and Sharer, J. S., "Analysis of Thermochemical Water-Splitting Cycles." Paper presented at T.H.E.M.E. Conference, Miami, March 1974.

15. Pangborn, J. and Gillis, J., "Alternative Fuels for Automotive Transportation – Feasibility Study." Vol. II, Chap. 8 of the Final Report on EPA Contract No. 68-01-2111, EPA-460/3-74-012. Chicago: Institute of Gas Technology, July 1974.

16. Pangborn, J. B. and Gregory, D. P., "Nuclear Energy Requirements for Hydrogen Production From Water." Paper presented at the Ninth I.E.C.E.C., San Francisco, August 1974.

17. Pangborn, J. B. and Greogry, D. P., "Evaluation of Thermochemical Hydrogen and Oxygen Formation From Water. Paper presented at the BNES International Conference, London, November 1974.

18. Quade, R. N. and McMain, A. T., "Hydrogen Production With a High-Temperature, Gas-Cooled Reactor (HTGR)," in Veziroglu, T. N., Ed., Hydrogen Energy, 137-54. New York: Plenum Press, 1975.

19. Schulten, R., von der Decken, C. B. and Barnert, H., "Nuclear Water Splitting by Heat From the Pebble Bed HTR." Paper No. 18, Session III of the British Nuclear Engineering Society International Conference on HTR and Process Applications, London, November 26-28, 1974.

20. Stevens Institute of Technology, "Hydrogen As A Fuel." Semiannu. Tech. Rep. Contract No. N00014-67-A-0202-0046, January-June, 1974.

21. U.S. Atomic Energy Commission, Forecast of Growth of Nuclear Power, Washington, D.C., 1972.

7. PRODUCTION OF HYDROGEN BY PHOTOSYNTHETIC PROCESSES — R. H. Elkins

Introduction and Problem Definition

Practically all of the energy required for the growth of our technological civilization up to this time has been ultimately supplied by the photosynthetic conversion of solar energy to cellulose and cell material that has been stored through the ages as fossil fuels. Faced with the rapid depletion of this source of energy, considerable attention is now being given to determining whether or not (and if so, to what extent) the photosynthetic process can be accelerated to meet current and future energy needs. The most fundamental problem is the inefficiency of solar energy conversion to chemical energy. With conventional plant growth, the efficiencies are generally quite low — only 0.5% to 2.0% of the total flux is converted to fixed carbon. As will be shown, there is no thermodynamic factor preventing attainment of efficiencies as high as 10% for hydrogen-producing photosynthetic processes.

Of course, most research activity in this area has centered on the more conventional approaches for accelerating the growth of plants and algae or on converting residues (particularly wastes such as human and animal sewage) to methane.[6,9,12,45,46,61] However, because the concept of a future hydrogen economy has received much attention, a number of proposals have been addressed specifically to the production of hydrogen by photosynthetic processes.[4,5,8,10,24,34,36,42,43] These ideas include not only the more conventional approach of converting carbonaceous photosynthetic residues to hydrogen by the action of nonphotosynthetic organisms or photosynthetic processes, but also (and more importantly) the direct photochemical splitting of water into hydrogen and oxygen. At this time, the proposals for direct water splitting are generally only research suggestions, so objective engineering evaluations are not possible at this time. Nevertheless, a brief analysis of the energetics of the photosynthetic process indicates that the process is, in fact, thermodynamically capable of producing hydrogen and oxygen from water.

In evaluating such proposals, it must be kept in mind that a number of methods already exist or can be developed by which the carbonaceous products of photosynthesis can be converted to hydrogen. Furthermore, the most fundamental problem remains the improvement of the efficiency at which solar energy can be converted to chemical energy, in whatever form. In this light, the problem becomes primarily one of evaluating —

- Whether or not photosynthesis has the potential to produce energy in amounts significantly in excess of our food requirements; and, if so, what research and development would be required to achieve that potential
- Whether hydrogen can be produced more efficiently directly by photosynthesis or indirectly from other photosynthetic products.

However, the evaluation of these points is still largely subjective and will differ even among the acknowledged "experts" in the field. Many in the field express considerable (but not universal) optimism that photosynthesis can be used as an efficient converter of solar energy, but only on a long-range basis. All acknowledge that breakthroughs will be required; but most agree that the effort is worthwhile, even if unsuccessful, because of the fundamental importance of a complete understanding of photosynthesis for possible application in increasing food production.

Historical Review of Photosynthesis Research[14,15,52]

Historically, the development of our understanding of photosynthesis has paralleled the development of chemistry as a science. By 1800, shortly after the discovery of oxygen by Priestley, the essential material balance for the process had been identified as –

$$CO_2 + H_2O \xrightarrow[\text{green plant}]{\text{light}} O_2 + \text{organic matter}$$

By 1845, coincident with his formulation of the law of conservation of energy, Mayer understood the essential energy balance, as well as the material balance of the process:

$$CO_2 + H_2O + \text{light energy} \rightarrow O_2 + \text{organic matter} + \text{chemical energy}$$

At this point, he realized the tremendous importance of photosynthesis as nature's primary means for storing solar energy.

Little progress was made toward understanding the mechanisms of this reaction until the 1930's, after Van Niel's comparative studies of photosynthesis in green plants and in photosynthetic bacteria. These bacteria, like green plants, utilize light energy for growth and contain an essential pigment, bacteriochlorophyll, which differs only slightly from green-plant chlorophyll (Chl). However, the bacteria do not evolve molecular oxygen, and their

photosynthetic growth depends on the presence of an oxidizable substrate such as hydrogen, hydrogen sulfide, or a variety of organic compounds (particularly the simpler alcohols and organic acids). To include these organisms, Van Neil formulated the photosynthesis reaction as an oxidation-reduction process:

$$CO_2 + 2H_2A \xrightarrow[Chl]{light} CH_2O + H_2O + 2A$$

in which H_2A represents a general class of oxidizable compounds and A is the product of its oxidation. Soon after this formulation it was realized that green-plant photosynthesis might be a special case in which the oxidizable substrate, H_2A, is water, which is oxidized tc oxygen. If so, the overall reaction of green-plant photosynthesis would be written –

$$CO_2 + 2H_2O \rightarrow CH_2O + H_2O + O_2$$

On this basis, Van Niel postulated that the primary photochemical event is the splitting of water to produce an oxidant, denoted (OH), and a reductant, denoted (H). In turn, the primary reductant would bring about the reduction of carbon dioxide to a carbohydrate, denoted as CH_2O, and the primary oxidant would react with H_2A:

(The primary oxidant and reductant were not regarded literally as hydrogen atoms and hydroxyl radicals, but rather as unspecified oxidizing and reducing species.)

Thus, the Van Niel hypothesis suggested that the unique event of photosynthesis was an oxidation-reduction reaction driven by chlorophyll in a photoactivated state. Since then, the oxidation-reduction nature of the process has been established beyond question.

The Energetics of Solar Radiation and the Thermodynamics of Photosynthesis[14,15,38,52]

The energetics of photosynthesis in nature are constrained by the nature of living matter and by the spectrum of sunlight reaching the earth's surface.

Most of the ultraviolet (UV) light below about 300 nm is absorbed by ozone in the upper atmosphere and never reaches the earth. Infrared radiation (IR) is absorbed by the water that universally surrounds living matter and by atmospheric water vapor, thus having no chemical effect. As a consequence, the range of wavelengths available for photosynthesis is from about 300 to 1300 nm.

In nature, every part of the spectrum from 300 to 950 nm is absorbed (and is thus available for utilization) by one organism or another. Green plants, in which photosynthesis involves the splitting of water, primarily absorb radiation in the visible range (from 400 to 700 nm). This represents about half of the total solar radiation that reaches the earth's surface: The other half is in the infrared range.

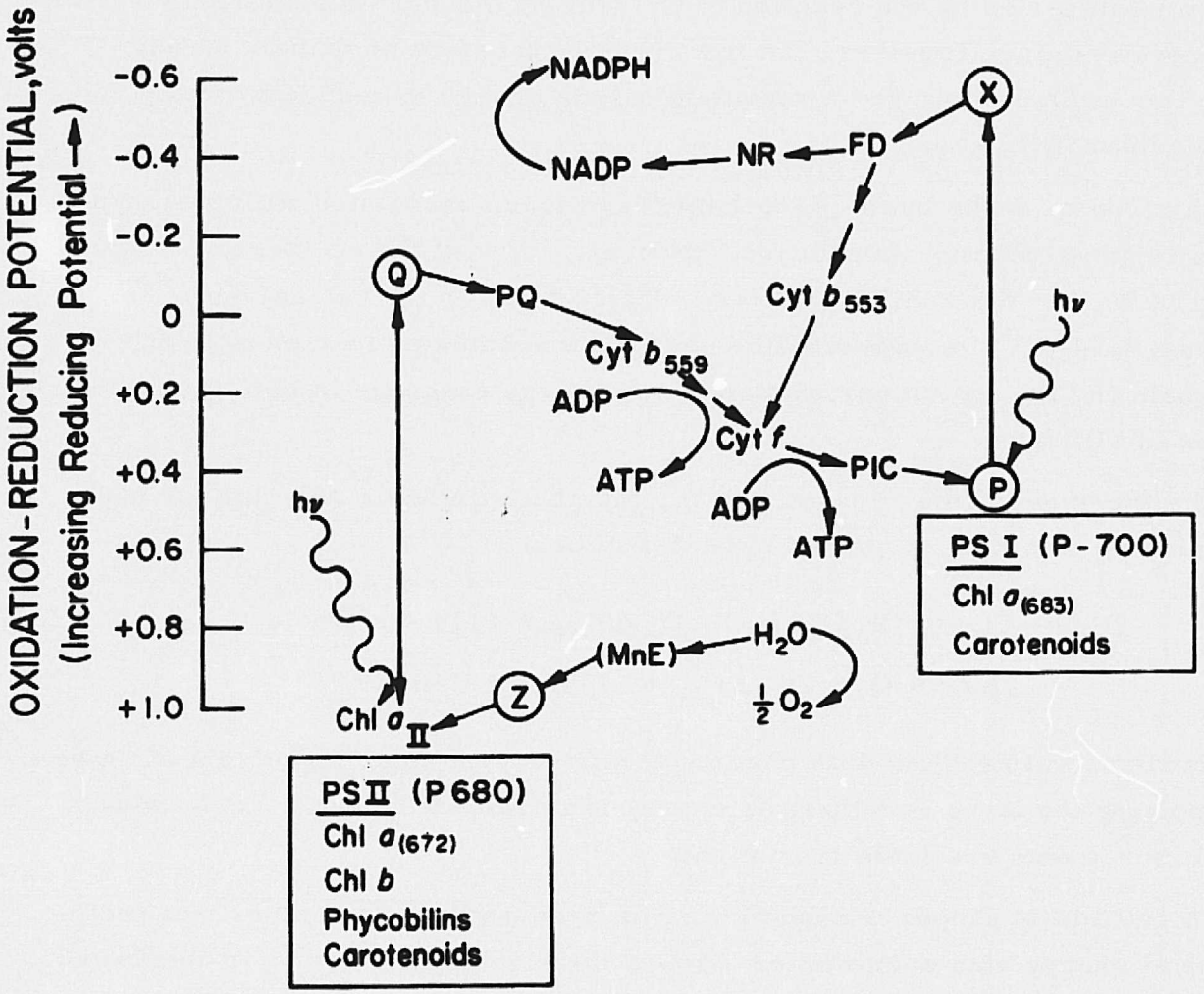
The energy content of light is inversely proportional to its wavelength, and the energy content of photons in the visible spectrum ranges from about 70 kcal/Einstein* at 400 nm to about 40 kcal/Einstein at 700 nm. Thus, the energy of the solar radiation available for photosynthesis is limited to the range of from 40 to 70 kcal/Einstein, far less than the energy required to break the oxygen-hydrogen bond (about 111 kcal/mole). Furthermore, efficient conversion of the absorbed solar energy requires its utilization in increments as small as 40 kcal/mole.

Series Model for Photosynthesis[14,15,23,38,52,63]

The series model, which came into vogue in the early 1960's, is shown in Figure 7-1. Essentially, this figure is a flow diagram of the electron transport during the photosynthetic process in the context of the electrochemical potential at which the electron exists (a measure of the energy of the electron, or its reducing power) at various stages of the process. Thus the ordinate denotes the chemical reducing power of the negative ion in which the electron resides, and the horizontal progression denotes the chronological or chemical sequence of the transport. The arrows show the direction of electron flow.

The photochemical reaction in photosystem II (PS II) generates a strong oxidant, Z^+, which is capable of liberating oxygen from water, and a weak reductant, Q^-. A second photochemical reaction, in photosystem I (PS I),

* 1 Einstein = 1 mole of photons.



MnE = hypothetical enzyme containing manganese
Z = hypothetical donor of electrons to oxidized Chl a (672)
Q = primary electron acceptor in the photochemistry of system II; may be a quinone
PQ = plastoquinone
PIC = plastocyanin
NR = NADP reductase
FD = ferredoxin
P = hypothetical donor to oxidized Chl a (683) if any

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Figure 7-1. TWO-QUANTUM-SERIES MODEL OF ELECTRON FLOW IN PHOTOSYNTHESIS

generates a weak oxidant, P^+, and a strong reductant, X^-, which has a potential more negative than that of the hydrogen electrode. The two systems are connected in series by the reaction of Q^- with P^+ through an elaborate electron-transport system. Together, the two systems generate an oxidant strong enough to oxidize water and a reductant strong enough to reduce hydrogen ions to molecular hydrogen.

This, then, is the basic phctochemical process associated with photosynthesis in green plants. In addition, however, some of the exothermic energy released by the "down-hill" electron transfer between the two halves of the process, $Q^- \longrightarrow P^+$, is converted by unknown mechanisms to adenosine triphosphate (ATP), the universal medium of energy exchange in biological processes of all kinds.

The thermodynamic requirement for the photosynthesis reaction (or for the splitting of water) is about 114 kcal/2 moles:

$$2H_2O + CO_2 \rightarrow CH_2O + H_2O + O_2 \quad \Delta F_{298} = +114 \text{ kcal/mole}$$

$$2H_2O \rightarrow O_2 + 2H_2 \quad \Delta F_{298} = +113.4 \text{ kcal/mole}$$

The fundamental problem with photosynthesis or with solar photolysis of water is supplying the large endothermic energy requirement from the relatively small increments available in sunlight.

To put this in proper perspective, it is necessary to remember that photochemical energy acts upon matter through the electrons on a one-to-one basis – i.e., the energy of one quantum of light is transferred (at varying efficiency) to one electron. In this sense then, the energy of a photon is analogous to electrochemical potential in that it represents the available free energy per electron rather than per mole of product. On this basis, 40 kcal/Einstein corresponds to an electrochemical potential of 1.74 volts,* which is more than sufficient to split water. (The theoretical voltage requirement for splitting water is 1.23 volts.)

The reduction of carbon dioxide to CH_2O and the evolution of oxygen from water are processes that involve the transfer of four electrons per molecule – i.e., the primary photochemical process must occur at least four times to

* 1 volt = 23.053 kcal.

reduce one carbon dioxide molecule and to evolve one oxygen molecule. On this basis, the quantum requirement for photosynthesis would be at least 4 quanta per molecule, if the primary reaction is driven by a single quantum as originally assumed. If this is the case, the thermodynamic efficiency would be about 71%.

In the early 1920's, experimental determinations by O. Warburg, using manometric techniques for the measurement of the oxygen and carbon dioxide, appeared to confirm that the quantum requirement for photosynthesis is four. However, more realistic estimates of the energy requirement, which include the probable thermodynamic losses in the process, suggested that the actual requirement must be in excess of 4 quanta per molecule. On this basis, the primary photochemical process would require at least 2 quanta of light for each electron – an overall minimum requirement of 8 quanta per molecule. This initiated a controversy that lasted 30 years. It was finally established that each electron transfer does, in fact, require two photochemical reactions for each electron – a total quantum requirement of eight per oxygen molecule evolved, thus indicating a thermodynamic efficiency limit of about 35%.

However, the problem was not then resolved by direct experimental measurement of the quantum requirements for oxygen and carbon dioxide exchange. Instead, the initial evidence for a two-quantum primary photochemical process came from a fascinating series of studies on the effect of monochromatic light of varying wavelength on the efficiency of photosynthesis. The results of these studies led to the Z scheme (or series model) of photosynthesis, which postulates that the primary photosynthetic process actually involves two separate photochemical systems that act cooperatively in series and that are connected by an electron-transport system that utilizes cytochromes. Furthermore, photosynthesis can occur only when both systems are operative, either simultaneously or consecutively. The overall photosynthesis reaction is then completed by coupling the photochemical reactions to the "dark" enzymatic reactions (i.e., those that occur in the dark) required to allow Z^+ to oxidize water to oxygen and X^- to reduce carbon dioxide to glucose.

Possible Approaches to Hydrogen Production

The above analysis indicates that it is theoretically possible to split water into hydrogen and oxygen if alternative processes can be found for the enzymatic reaction of X^-. Although it appears to be universally true

that the reducing power, X^-, generated by green-plant photosynthesis is always used to reduce carbon dioxide to cell material, biological hydrogen production by photochemical processes, as well as dark processes, has been observed. The study of these processes has resulted in the suggestion of a number of approaches to photosynthetic hydrogen production.

Hydrogen Production by Natural Biological Processes[25]

Certain bacteria and algae contain enzymes, such as hydrogenase, and are capable of catalyzing the reduction of hydrogen ions to molecular hydrogen.[7,19,25,33,59] Such organisms do, in fact, product hydrogen under certain conditions by photochemical reactions, as well as by the dark reactions.

Hydrogen is produced by a number of anaerobic microorganisms, notably the Clostridium types, during the anaerobic metabolism (fermentation) of carbohydrate. The hydrogen donor in these systems is organic and is usually formic or pyruvic acid, intermediates in fermentation.[25] Thus hydrogen is actually produced as a by-product.

Hydrogen can also be produced by a number of photosynthetic bacteria that contain nitrogenase, an enzyme for fixing nitrogen.[25] However, hydrogen is only produced by growing cells in the absence of nitrogen and by certain nitrogen metabolites on a substrate such as glutamic acid, which contains both the nitrogen and carbon required for growth. Cells in the resting stage, however, can produce hydrogen almost quantitatively from substrates such as acetic, succinic, and malic acid:

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Thus in the case of photosynthetic bacteria, the hydrogen donor for hydrogen production is also primarily organic, and no species has been found in which water is the ultimate source of the hydrogen produced. This is consistent with the fact that photosynthetic bacteria do not incorporate photosystem II.

Until recently, no case had been found in which water was the substrate or in which PS II participated[7,59]; but certain algae, containing hydrogenase or nitrogenase, have been found that, after anaerobic adaptation, do produce hydrogen photochemically.[19] Because the algae show photosystem-II activity, the possibility exists that water could be the source of the hydrogen produced. In all cases, however, the rates of photohydrogen production have been very slow compared with the rates of photosynthesis.[7,33,59]

Still, the biochemical mechanisms involved in biological hydrogen production are not well understood. The process appears to be primarily associated with anaerobic conditions and processes. (Hydrogenase is oxygen sensitive.) Its function appears to be regulatory in nature. Gray and Gest state [25]:

> "In heterotrophic organisms, the anaerobic mode of growth poses special problems for the cell with respect to the disposition of electrons from energy-yielding oxidation reactions. This is particularly so when the overall adenosine triphosphate (ATP) requirement for biosynthetic activity can be satisfied only by degradation of a relatively large quantity of an organic compound that serves as the energy source. Accordingly, various kinds of specific controls are necessary to regulate electron flow in the metabolism of strict and facultative anaerobes. One of these is reflected by the ability of many such organisms to dispose of excess electrons in the form of such molecular hydrogen (H_2) through the activity of hydrogenases, which, in effect, catalyze the reaction:
>
> $$2e^- + 2H^+ \rightarrow H_2$$
>
> From a general standpoint, the formation of molecular hydrogen can be considered a device for disposal of electrons released in metabolic oxidations."

Kok also suggests [33] that the function of hydrogen formation in algae is to "prime the photochemical pump under anaerobic conditions." He further suggests that algae frequently encounter anaerobic conditions under which the photosynthetic electron-transport chain is reduced, thus effectively blocking flow. However, utilization of the electrons to reduce hydrogen ions effectively primes the pump by converting the electron-transport system back to the oxidized state, thus allowing photosynthesis to proceed. Land plants, on the other hand, never encounter anaerobic conditions and thus contain no hydrogenase.

Thus the hydrogen-production mechanism does exist in photosynthetic bacteria and in algae, but its function is regulatory rather than primary in nature. Indeed, an organism in which the photosynthetic apparatus has been subverted to produce hydrogen rather than cell material can no longer be considered a viable, self-reproducing system. Furthermore, the aerobic water-splitting and anaerobic hydrogen-production functions are not compatible because hydrogenase is highly oxygen sensitive. Thus it would appear that the direct production of hydrogen and oxygen from water by living organisms has a very low probability of success.

Recently, however, a nitrogen-fixing algae species, Anabaena cylindrica, has been found that under certain conditions does, in fact, evolve oxygen and hydrogen simultaneously under the influence of light while in a growth stage.[5] This discovery could be important, if not as the basis for solar conversion, at least as a guide to how it might be accomplished in vitro.

Anabaena cylindrica is a heterocystic filamentous nitrogen-fixing alga in which the nitrogenase activity apparently exists in distinctly differentiated cells located at intervals among the vegetative cells of the filament. In the vegetative cells, photosynthesis occurs as usual, splitting water to produce oxygen and, with carbon dioxide, cell material. However, some of the carbohydrate so produced is supplied to the nitrogenase containing cells (heterocysts) as feedstock for photosynthetic nitrogen fixing. Thus the two types of cells have a symbiotic relationship.

Typical of nitrogen-fixing species is that hydrogen, rather than fixed nitrogen (ammonia) is produced when nitrogen is excluded.[5, 25, 26] Because nitrogenase is oxygen sensitive, nature apparently developed heterocysts to separate the aerobic photosynthetic process from the anaerobic nitrogen fixing. Thus both oxygen evolution and hydrogen (ammonia) production can coexist in the same organism, although in different cells.[5]

Usually oxygen production is several times greater than nitrogen production. However, after several days of nitrogen starvation, oxygen production decreases, and hydrogen production increases. Thus it may be possible to control the stoichiometry -- unfortunately, however, at the expense of solar-conversion efficiency.[5] It is presumed also that a nitrogen nutrient would have to be supplied. On the other hand, it may be possible to find or to develop genetically improved strains.

Similar possibilities exist for certain plant-nitrogen fixing algae systems that normally live in symbiotic relationship. One such system consists of Anabaena azollae, a blue-green algae, and Azolla, a genus of water ferns. This system has been used in Asia as a fertilizer and as animal food, and nitrogen-fixing rates of up to 125 lbs/yr-acre have been reported. Recently G. A. Peters (of Kettering Research Laboratory) has shown that the algae, when separated from the fern, continues to fix nitrogen for up to 12 hours at a somewhat reduced rate and without further growth.[51] Thus it appears that the algae depends upon the fern for at least some of its nutrients (presumably

carbohydrate) and supplies its partner with nitrogen. It might be possible, with such systems, to control the hydrogen-oxygen stoichiomery under nitrogen-starvation conditions by controlling the relative algae/fern ratio. Again it would be necessary to provide nutrient nitrogen.

The Nature and Efficiency of Nitrogenase Reductions

There has been considerable research on biological nitrogen fixing for the production of ammonia, as well as of hydrogen, since 1960 (when nitrogenase was first isolated).[26,40] However, the nature of nitrogenase and the reaction mechanisms involved are not well understood.[26,65] Both ATP and an energy-rich substrate, such as pyruvate or possibly reduced nicotinamide-adenine dinucleotide phosphate (NADPH), are required. The reductive input to the system appears to involve an iron-containing enzyme similar to the ferredoxins that mediate the reduction of nicotinamide-adenine dinucleotide phosphate (NADP) to NADPH in photosynthesis. Nitrogenase is also a complex enzyme, containing both iron and molybdenum. The system is remarkably versatile in that it can bring about the reduction not only of nitrogen and hydrogen ions, but also of a variety of unsaturated compounds, such as that of acetylene to ethylene.[26] The acetylene reduction is used as a quantitative monitor of nitrogen-fixing rates.

Unfortunately, the nitrogen-fixing reaction is extremely inefficient. Hardy and Havelk estimate[26] that a minimum of 24 moles of ATP are required for the reduction of one molecule of nitrogen. As a result, it has been estimated that almost 20% of the photosynthate produced by ligumes is used by the associated nitrogen-fixing species to fix nitrogen. Thus ammonia or hydrogen production is apparently accomplished at a high cost to the efficiency of photosynthesis, at least in natural symbiotic systems. (No efficiency data were given by Beneman[5] for the heterocystic-algae case.)

Genetic Engineering

A number of suggestions have been put forth concerning the use of "genetic engineering" for developing strains of organisms or plants to solve many of these problems. Certainly, the genetic approach has had some spectacular successes in bringing about the "green revolution" in conventional agriculture. Until recently, however, these techniques had been aimed primarily at increasing food and lumber production.[11,64] Broadening of the genetic approach to include energy production is obviously justified.

Proposals to develop mutant, or "engineered," organisms to produce stored energy in a form other than cell material are much more difficult to evaluate.[7,34,44,58,60,62] First, the science of molecular genetic manipulation is in its infancy, and evaluating the chances of success is difficult. Second, such organisms, if developed, would not be growing, self-repairing, self-reproducing systems and therefore would require maintenance and stabilization.

The possibility does exist, however, that such systems may be amenable to stabilization for long "catalyst" life. Furthermore, the "spinoff" results from such studies may contribute to the development of high-efficiency converters of solar energy to more conventional cell-material energy.

In Vitro Processes

The feasibility of coupling the hydrogenase (and nitrogenase) activity to the photosynthetic process PS I in green-plant chloroplasts was demonstrated in the laboratory as early as 1961.[1] However, in these experiments, PS II activity, and therefore oxygen evolution, was effectively blocked; and an artificial electron donor was substituted.

By 1973, however, Benemann et al.[4] actually demonstrated that hydrogenase activity can, in fact, be coupled to the photosynthetic apparatus of green plants to produce hydrogen and oxygen in the laboratory. Inhibition of the hydrogenase activity by the oxygen produced was minimized by continuous flushing with argon. However, the rates of hydrogen evolution were relatively slow compared with those in experiments in which oxygen evolution was blocked (by inhibition of PS II and substitution of an artifical electron donor) or scavenged by glucose oxidase. The results indicated that the oxygen inhibition of both hydrogenase and ferredoxin is a problem that must be solved before further development can proceed.

Since 1973, Kaplan has been able to purify Clostridium hydrogenase and immobilize it on glass surfaces.[29] In the immobilized form, the hydrogenase appears to be stable in the presence of oxygen. Similar suggestions have been made by various workers in the field.

Another approach to coupling hydrogenase to photosynthesis has been suggested by L. O. Krampitz at Case Western Reserve University.[34,36] Instead of direct coupling, he suggests that the photosynthetic apparatus of

green plants be used to produce a stable reduced species (in the absence of carbon dioxide) that can be converted to hydrogen by hydrogenase in a second step, without the inhibiting effect of oxygen. Again, the feasibility of this approach has been demonstrated in the laboratory with triphosphopyridine nucleotide (TPN) as the electron acceptor. TPN is an alternative term for NADP – the natural hydrogen acceptor in photosynthesis that, in the reduced form, mediates the reduction of carbon dioxide. It is a fairly complex, but stable, chemical species.

In the first-stage reaction, TPN was added to a suspension of spinach chloroplasts and ferredoxin, which was then illuminated. The reaction produced oxygen and reduced triphosphopyridine nucleotide (TPNH). The TPNH was then subjected to Clostridium hydrogenase and ferredoxin, in a second-stage reaction, to evolve hydrogen. Thus the feasibility of a two-stage process was demonstrated in terms of a fairly complex biological chemical:

$$H_2O + TPN \xrightarrow[Chl]{h\nu} 1/2O_2 + TPNH_2$$

$$TPNH_2 \xrightarrow{\text{hydrogenase}} TPN + H_2$$

Obviously, a simpler, more stable first-stage electron acceptor is desirable and is being sought.[34]

It is apparent that hydrogen can be thermochemically produced from any stable, reduced product of photosynthesis. The most obvious thermochemical process would involve the use of natural photosynthetic products (such as carbohydrate) to reduce water. However, other possibilities exist. For example, it has been known since 1937 that slurries of chloroplasts (isolated from green leaves) with a suitable electron acceptor, such as benzoquinone, will evolve oxygen and yield hydroquinone when illuminated with visible light (the Hill reaction).[15,52] Thus, the following two-stage, water-splitting cycle can be visualized:

$$2H_2O + 2Q \xrightarrow{h\nu} 2QH_2 + O_2$$

$$2QH_2 \xrightarrow[\text{catalyst}]{} 2Q + 2H_2$$

Unfortunately, only a portion of the total reducing power of the photosynthetic apparatus (that is, only PS II) is utilized in the Hill reaction. However, the reducing power of the whole photosystem is available, as shown in the studies by Krampitz[4] and Benemann et al.[34] Thus it may be possible to find a terminal oxidant for photosynthesis that yields a stable reduced species from which hydrogen can be produced by a thermochemical second stage.

Cell-Free Reconstituted Systems[42,43,59]

Understanding of the photosynthesis process and biological hydrogen formation is sufficient to have stimulated proposals for in vitro systems reconstituted from the various components of the natural systems. In this way it might be possible to physically separate the aerobic and anaerobic functions. However, because membrane structures and coupling mechanisms are two large unknowns at this time, the potential for this approach lies in the future. Also, because these then are no longer living, growing species, maintenance or stabilization of the very complex, delicately balanced system becomes of paramount importance.

As we have seen, the stabilization of hydrogenase appears to have been accomplished.[29] However, stabilization of the photosynthetic system will presumably present a much more difficult problem. Unfortunately, the photosynthetic systems in chloroplasts are, for reasons unknown, highly degradable, so the Hill reaction lasts only a few minutes. Similar photolytic catalysts with improved stability can be prepared simply by lyophilization of whole photosynthetic bacteria or algae. These preparations have shelf stabilities of up to 1 year, and their catalyst life is increased from a few minutes to a few hours.[35]

Stabilization of the photocatalytic system is now recognized, in the field, as a high-priority goal.[46] However, this recognition has come only recently, with the realization of the energy crisis. Thus, work toward this goal is just beginning.

Two-Stage Photochemical and Fermentation Processes

Fermentation of Photosynthetic Residues

Obviously, it is possible to produce hydrogen and oxygen from water by a conventional two-stage process with living and growing organisms — that is,

by the secondary conversion of photosynthetic marine or agricultural residues to hydrogen by anaerobic fermentation or by the action of photosynthetic bacteria. Such processes have been proposed,[34,36] and hydrogen production by fermentation with clostridial species actually has been performed commercially.[3] However, hydrogen is produced in such processes only as a by-product of the primary production of alcohols, ketones, or fatty acids. Presumably, better strains could be developed to maximize hydrogen production. Also by-product alcohols and fatty acids might be converted to hydrogen in separate reactions by other bacteria. However, such processes would merely represent alternative methods for converting primary photosynthetic products to useful fuels such as methane or cellulose. Furthermore, methane processes are much closer to commercial feasibility. Wolfe believes[20] that a relatively modest investment (~ $1 million) in basic research on methane fermentation would result in substantial technical and economic improvement.

We do not discount the potential for hydrogen or methane production from carbonaceous photosynthetic residues, particularly those that would otherwise be waste materials (e.g., sewage or garbage). However, this potential is ultimately subject to the basic limitations on the efficiency at which solar energy can be converted in marine and agricultural residues to feedstock for hydrogen or methane production.

Nonbiological Photolysis

It seems likely that nonbiological water photolysis that utilizes a substantial portion of the available solar flux will require the coupling of two or more photocatalytic (or stoichiometric) reactions in a closed cycle in order to bridge the energy gap. In photosynthesis, two photochemical processes are coupled "in series" via an elaborate electron-transport chain so that a net electrochemical potential of about 1.2 to 1.4 volts is imparted to each electron involved, and the reaction is accomplished in one integrated step. It may be possible to accomplish this in the laboratory, but at present it appears difficult.

There are, however, other ways to accomplish the same objectives. For example, it should be possible to electrochemically couple certain photochemical reactions. In particular, the overall potential needed for splitting water might be provided in smaller increments by coupling two or more electrochemical cells in series.

Fujishima and Honda have demonstrated[18] an effective means for coupling the photochemical sensitization of n-type semiconductors to the production of hydrogen and oxygen from water. This was accomplished simply by using the irradiated titanium dioxide (TiO_2) semiconductor as the anode of an electrochemical cell in series with a platinum-block cathode. The photochemical and electrode reactions are presumed to be as follows:

$$4h\nu \xrightarrow[TiO_2]{} 4p^+ + 4e^-$$

$$4p^+ + 2H_2O \rightarrow O_2 + 4H^+ \qquad -1.23 \text{ V}$$

$$4e^- + 4H^+ \rightarrow 2H_2 \qquad 0.0 \text{ V}$$

$$4h\nu + 2H_2O \rightarrow O_2 + 2H_2 \qquad +0.5 \text{ V}$$

The anode was irradiated with 415 nm light (~3.0 volts), corresponding to the band gap of TiO_2. The electromotive force (EMF) of the completed cell was 0.5 volt. Thus, the photochemical reaction must have generated an electrochemical potential of 1.73 volts (1.23 + 0.5). This corresponds to a quantum-energy-conversion efficiency of about 58% (about the same as in photosynthesis). Unfortunately, the quantum efficiency was only about 10%, and the process can utilize less than 10% of the solar spectrum. However, the experiment is important because it illustrates a practical method of utilizing photochemically generated electrochemical potential.

This approach is also being studied in a NASA-sponsored program at M.I.T. under the direction of M. S. Wrighton.[47] Their work, in general, confirms the work of Fujishima and Honda, although the electrolysis actually requires a 0.2-volt assist. This program will explore TiO_2 and other semiconductor systems, as well as other variables in the system.

Similarly, other photocatalyzed reactions could be used as half-cell components of an electrochemical cell. Unfortunately, however, the potential generated by photocatalytic reactions that utilize significantly longer wavelengths of light will not be sufficient to split water. Such reactions do, however, result in the storage of energy or in the generation of electrochemical potential. The problem then becomes one of coupling the incremental energies generated by the partial reactions into a multistage process that will result in the splitting of water.

Ohta and Kamiya have suggested[48] that electrochemical potentials of less than 1.23 volts can be used to assist the electrolysis of water by conventionally generated electricity. For example methylene blue (MB) and ferrous ions generate an electrochemical potential of about 0.2 volt when irradiated:

$$2Fe^{++} + H^{+} + MB^{+} \xrightarrow{h\nu} 2Fe^{+++} + MBH$$

If such a cell were placed in series with a water electrolysis cell, the potential required for electrolysis would be reduced by about 0.2 volt – a rather small assist. Alternatively, it might be possible to use a stack of eight such cells in series to generate a potential of 1.6 volts (ignoring overvoltage), which would be sufficient for the electrolysis of water. However, the solar-energy-conversion efficiency would be reduced to a maximum of about 7% of the absorbed energy.

Ohta and Kamiya have also demonstrated that three complex dye systems in series can generate significantly greater EMF values (~ 0.6 volt) and a negative potential at the anode close to that of the hydrogen electrode. Thus they have a prototype for an anode that is almost capable of reducing hydrogen ions to molecular hydrogen. Their paper, however, did not give detail sufficient for evaluation of whether this series utilizes one or two photons per electron. If it is a two-photon event, the solar-energy-conversion efficiency is probably no greater than that for each individual cell. In any case, only the anode portion of the cell was studied. Thus coupling into a complete electrochemical cell has not been achieved.

On the other hand, to our knowledge, none of the photochemical reactions discovered thus far appear to be able to generate an oxidant strong enough to liberate oxygen at the cathode (utilizing the longer wavelengths of light). However, the approach is valid, although on the basis of current knowledge, such processes will probably be very complex, as illustrated by the proposal by Graves and Stramonde[24] that utilizes three half-cell reactions based on organic dyes (one with a cyctochrome redox system), hydrogenase to evolve hydrogen, and a six-stage thermochemical cycle to evolve oxygen. Obviously, photochemical half-cell reactions that are capable of bridging a much larger portion of the 1.23-volt energy gap are needed. This would increase efficiency, as well as simplify the coupling problem.

Efficiency of Solar Utilization[32,33]

The Basic Photosynthetic Process

Ideally, the above formulation indicates that photosynthesis utilizes 8 Einsteins of light at an energy of 40.8 kcal/Einstein to produce the free-energy equivalent of 2 moles of hydrogen plus 1 mole of oxygen. Thus the maximum internal thermodynamic efficiency of the process is about 35% [114 kcal/(40.8 X 8)] of the energy received by the reaction center. In actuality, however, the reduction of carbon dioxide to carbohydrate requires about 4 molecules of ATP, in addition to the light-generated reducing function (NADPH).[15] About half of the ATP requirement is generated by the exergonic electron-transport system at no cost in light energy. The other half, however, is generated by photophosphorylation and apparently requires two extra quanta of light. The maximum thermodynamic efficiency for producing carbohydrate, therefore, is actually closer to 28% of the energy received.

These calculations are in agreement with similar estimates made on the basis of charge separation produced by 700-nm light (~ 1.77 volt). Thus, at an efficiency of 56%, 700-nm light produces a charge separation of about 1 volt. A total of two quanta, at 1.77 volts each, produces a net charge separation of about 1.23 volts — an overall efficiency of about 35%. Thus the thermodynamic efficiency at which the process utilizes the energy delivered to the reaction center is relatively high.

To convert the above efficiencies to solar-utilization efficiency, we must allow for two other factors:

- In order to utilize light energy at a constant 1.77 volts, higher energy photons have been degraded to that level. The average wavelength of the light absorbed is about 550 nm, which corresponds to an energy of 2.25 volts (or 52 kcal/Einstein).
- Only about 45% of the solar spectrum is in the 400 to 700-nm range.

Taking these two factors into account, the actual maximum utilization efficiency should be 22% [114/(10 X 52)] of the light absorbed, or about 10% of the total solar flux. There appears to be a considerable amount of experimental confirmation of the order of magnitude of this value. Kok states[33] that "algae and higher plants have been grown (in weak light) with efficiencies approaching this value — converting 20% of the absorbed solar radiation (~ 550 nm)." Of course, this is under ideal laboratory conditions. However,

solar-utilization efficiencies as high as from 5% to 6% have been measured on a daily basis, under field conditions, for crops such as corn and sugar cane.[39, 56] Thus a maximum practical efficiency of 10% does seem reasonable.

Marine and Agricultural Photosynthesis[39 56]

The solar utilization efficiencies found in nature, on the other hand, are substantially lower that 10%. Kok states[33] that "net production in the field seldom exceeds 2%; typical values are 0.5% to 1.5% (3 to 10 kW/acre)." However, he indicates that annual efficiencies of from 4% to 5% have been observed and cites efficiencies of ~3% for sugar cane and ~2% for forestry on the south coastal plains. Loomis et al.,[39] as well as Schneider,[56] generally confirm the order of magnitude of the above-quoted efficiencies, on an annual basis, for a number of crops. However, both show data indicating that daily efficiencies that approach 6% can be achieved with certain crops, such as corn, sugar cane, and tropical grasses. It is significant that, although the highest daily efficiencies for corn and sugar cane are about the same, the annual efficiency for sugar cane is about twice that for corn because of the length of the growing season. Thus annual efficiencies tend to be higher nearer the equator. It seems probable that annual efficiencies might actually approach the average daily efficiencies if cropping could be carried out on a continuous basis rather than in batches. Examples would include mixed natural ecosystems, such as the tropical rain forests, and a continuous algae-growth process.

The loss mechanisms have been summarized by Schneider[56] and by Loomis.[11] Many losses (e.g., those due to the density of the ground coverage, grazing and insects, or lack of nutrients) can be controlled by agricultural practice. Other losses, however, are more intrinsic to the photosynthetic process itself or to the overall plant physiology. These include—

- In strong light, limitation of the velocity by the dark enzymatic reaction (most plants attaining saturation of photosynthesis at intensities below that of noon sunlight)[52]
- In weak light, a decrease in net efficiency brought about by respiration and other factors[33]
- Further limitation of the maximum rates by the availability of water; organic nutrients (such as nitrate ions, NO_3^-); and, in particular, carbon dioxide
- Consumption by plants of a significant fraction of their gross production (< 50%) for their own maintenance (respiration)[64]

Each of these factors, particularly photorespiration and light-saturation intensity, varies considerably among different plants. Thus plant breeding and genetic manipulation could lead to significant improvements in the efficiency of photosynthesis in practice.[64]

Potential Efficiencies of Artifical In-Vitro Processes

Reconstituted in vitro photosynthesis, if it could be developed, could eliminate the need for respiration, as well as ATP formation. This would reduce the quantum requirement from 10 to 8 Einsteins per mole of oxygen evolved and would increase the theoretical maximum efficiency to 13.7% of the solar flux. Furthermore, because such processes could be carried out on a continuous (rather than batch) basis, the annual efficiencies would approach maximum. On the other hand, the energy required for control and maintenance of such systems would certainly reduce the overall efficiency.

Current Status and Future Prospects of Photosynthesis Research

The photosynthesis model presented in Figure 7-1 is consistent with the known experimental data, although other models can probably be devised to explain the same data. Clayton suggests[19] that the figure is a reasonable consensus as of 1970. However, the model, as it stands, is still incomplete. The general state-of-the-art and the problems yet unsolved are discussed below.

Electron-Transport System[14,15,52]

The electron-transport system connecting the two photochemical half-cell reactions has been fairly well elucidated.[14,15,52] The detail presented in Figure 7-1 primarily serves to illustrate the complexity of the transport chain. Each of the electron carriers shown (and there are probably more) is a complex chemical entity attached to or in the form of a protein. Furthermore, the relative amounts of the carriers vary. For example, there are 10 equivalent of PQ for every Q, two equivalent of cyt b_{559} for every cyt f, and one of PIC for every P_{700}. Thus the difficulties that might be anticipated in trying to stabilize such a system for use in vitro or in trying to construct a synthetic electron-transport system become evident.

Carbon Dioxide Reduction [21,22]

The ultimate electron acceptor in the photosynthesis process is actually NADP, a complex biological chemical. As indicated in Figure 7-1, NADP is reduced by the photochemical reductant, X^-, through a second electron-transport chain involving several more complex enzyme species, including an iron-containing ferredoxin. Although the sequence of these carriers has been reasonably well established, the nature of the photochemically produced reductant itself is unknown. Furthermore, the manner in which the electron-transport chain is coupled to the primary reductant is still a mystery.

NADPH (the reduced form of NADP) and ATP reduce carbon dioxide to carbohydrate. This process has been named the Calvin-Benson cycle: Elucidation of the mechanisms involved in the reduction earned Calvin and his associates at Berkeley a Nobel Prize.

Oxygen Evolution and PS II [13,16,52]

The electron donors and acceptors immediately surrounding chlorophyll a in PS II remain unidentified. The electron acceptor, Q, is presumed to be a quinone. Even less is known about the nature of Z (the oxidizing agent) and the reactions and reactants mediating the oxidation of water to oxygen. (It is known that manganese and chloride ions are somehow involved because extraction thereof effectively stops oxygen evolution.)

The generation of oxygen is one of the more critical steps in the whole process because it involves the molecular mechanism by which a chemical process is coupled to a photoactive membrane system (which, incidentally, can be synthesized in the laboratory [30]). Thus, if we knew how to couple such a membrane to a chemical or voltaic process, photosynthesis might be reproducible in the laboratory. In any case, the lack of analytical success suggests that a greater emphasis should be placed on the synthetic approach.

Stoichiometric Pathways [15,32]

The model, as currently formulated accounts for a single-electron process. However, the release of one oxygen molecule requires the accumulation of four electrons at a specific energy level. How this is accomplished is not well understood. Again this emphasizes the complexities, as well as the lack of understanding, of the mechanism by which a chemical reaction is coupled to the primary photochemical species.

Photophosphorylation [15,38,41,49,52]

In addition to the production of reducing power (NADPH), photosynthesis also results in the storage of energy in the form of ATP, which is the universal medium of energy exchange in biological processes. Although we are primarily interested in the reducing power generated by the photosynthetic process, consideration of the mechanism by which the phosphorylation process is coupled to the electron-transport system may lead to a better understanding of the process as a whole.

Phosphorylation appears to be of vital importance to many or all membrane processes in which active ion-transport occurs. In 1970, A. L. Lehninger stated [55]:

> "There can be no doubt that the most central and overriding problem we face today in the study of photosynthesis and respiration is the nature of the chemical and physical events involved in the conversion of electron-transport energy into phosphate bond energy. In both processes we have chains of electron-carrying proteins which are fixed in membranes, the structure of which is vital for their function. In both cases electron transport can lead not only to ATP formation, but also to transport of ions as H^+ across the membrane..."

Until recently, it was assumed that the coupling is chemical in nature, although the required chemical intermediates have never been identified. Furthermore, the chemical coupling hypothesis does not explain the necessity of a membrane structure for functionality.

More recently, P. Mitchell proposed [41] that the coupling occurs not through chemical intermediates, but rather occurs because of the electrochemical state of the membrane in which the electron-transport system is arrayed. This view, called the chemiosmotic hypothesis, postulates that electron transport occurs in a chain of geometrically oriented carriers within the membrane and is stoichiometrically related to the transport of hydroxyl ions across the membrane, which separates the inner and outer phases. Thus, an electrochemical potential, estimated to be on the order of 0.3 volt (quite sufficient to drive the ATP formation), is generated. [15,54]

Experiments show that illumination of chloroplasts is associated with a difference in pH across the membrane, as well as with ATP formation. Furthermore, Racker and Stoeckenius [53] (at Cornell) have reconstituted

membranes from the photosynthetic pigment of purple bacteria with an ATP enzyme from heart mitochondria that, when illuminated, generate a hydrogen ion gradient and ATP.

Whether the Mitchell hypothesis is basically correct in its present form or not remains unresolved.[38,49,57] However, it has served to focus attention on the importance of the membrane structure and dynamics and on biological membranes as energy transducers. In particular, the Mitchell hypothesis emphasizes our lack of understanding of the relationships between biological-membrane structure and function.

Nature of the Photosynthetic Unit[14,15,52]

The most fundamental, as well as the most important, unknown in the current understanding of photosynthesis is the nature of the photosynthetic unit itself in terms of structure and function. The primary photoacceptors in photosynthetic organisms belong to a small family of closely related pigments known as the chlorophylls. The principal members of this family are chlorophyll a and b (Chl a and Chl b) in green plants and algae and bacteriochlorophyll (BChl) in photosynthetic bacteria. Without exception, Chl a is present in all organisms that carry out photosynthesis with the evolution of oxygen. Although the chlorophylls appear to be the primary and essential components of the system, they are in nature associated with a number of other pigments, including the carotenoids and the phycobilins (phycoerythrin and phycocyanin). Together, these pigments absorb most of the visible spectrum of solar radiation. (See Figure 7-2.)

According to current views, the basic photosynthetic unit consists of about 300 to 400 molecules of Chl a, together with the associated pigments (most of which function only to "harvest" light and to transfer energy to a reaction center within the unit). The efficiency of the energy-transfer process is in excess of 90%.

The brief survey of nonbiological photolysis serves to highlight the unique properties of the chlorophyll photosensitizer in photosynthesis, in particular –

- Its ability to harvest light over the whole solar spectrum and to transfer the energy efficiently to the reaction center
- The photocatalytic nature of the reaction centers and the efficiency with which they convert photoenergy to electrochemical potential.

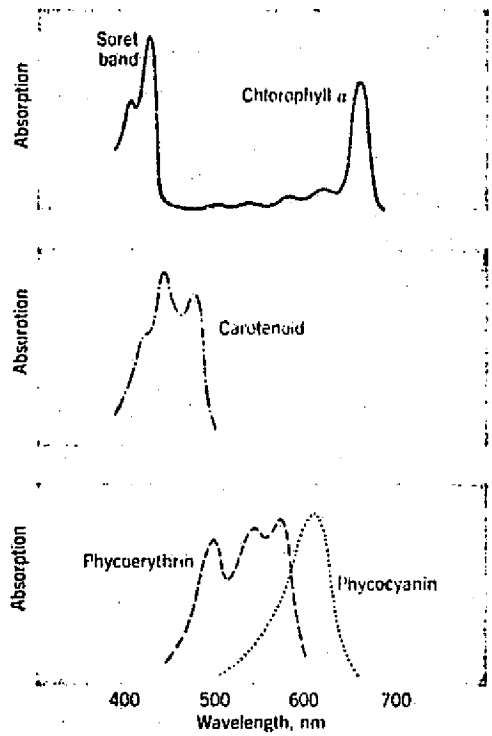

Figure 7-2. ABSORPTION SPECTRA OF THE THREE TYPES OF PLANT PIGMENTS

These properties appear to exist in nature only in photosynthesis, and both are derived from the nature of the chlorophyll molecule.

Of particular interest is the contrast between the photochemical reactions of chlorophyll in solution with those occurring in photosynthesis. For example, Chl a in methanol is photooxidized by suitable electron acceptors — such as Fe^{+++}, quinone, and a variety of dyes — in reactions reminiscent of the Hill reaction[52]:

$$\text{Chl } \underline{a} + Fe^{+++} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} \text{Chl } \underline{a}^{+} + Fe^{++}$$

or

$$2\text{Chl } \underline{a} + Q \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} 2\text{Chl } \underline{a}^{+} + QH_2$$

However, the reactions are stoichiometric, and the oxidized chlorophyll species does not appear to be reactive with water. Furthermore, the overall electrochemical potential bridged appears to be on the order of only 0.1 to 0.2 volt.

Similary, Chl a can be photoreduced by certain electron donors, such as ascorbic acid ($E_0 \cong 0.0$), in a reaction analogous to the Krasnovsky reaction[37 52]:

$$\text{Chl a} + \text{ascorbic acid} \xrightarrow[\text{dark}]{h\nu} \text{ChlH}_2 + \text{dehydroascorbic acid}$$

Again the reaction tends to be stoichiometric, although $ChlH_2$ can be reoxidized by various electron acceptors with electrochemical potentials of up to 0.02 volt. Thus the maximum energy stored is only 0.2 volt.

In contrast, each chlorophyll reaction center in photosynthesis generates a charge separation of about 1.0 volt at an efficiency of about 56% (1/1.77), and the process is photocatalytic. This accomplishment has only been partially explained, but considerable progress toward understanding the process has been made during the last 5 years.

Structure and Function of Chlorophyll

Chlorophyll a is a fascinating member of the porphyrin family. It consists of a cyclic tetrapyrrole chelated with magnesium. (See Figure 7-3.) In addition, the structure includes the following important features:

- An alicyclic ketone structure fused to one of the pyrrole rings, which appears to be conjugated to the unsaturated double-bond structures throughout the molecules
- An aliphatic acid group esterified with a 20-carbon-atom aliphatic alcohol.

The overall molecule is polar and hydrophilic at one end and nonpolar and hydrophobic at the other end. This strongly affects its colloidal behavior, particularly in nonpolar solvents and at polar-nonpolar interfaces. However, the most important and distinctive feature of the chlorophylls is that they contain both an electron-donor and an electron-acceptor function within the same molecule.

The central magnesium atom is constrained by the cyclic tetrahydropyrrole structure to a coordination number of 4 and is therefore coordinatively

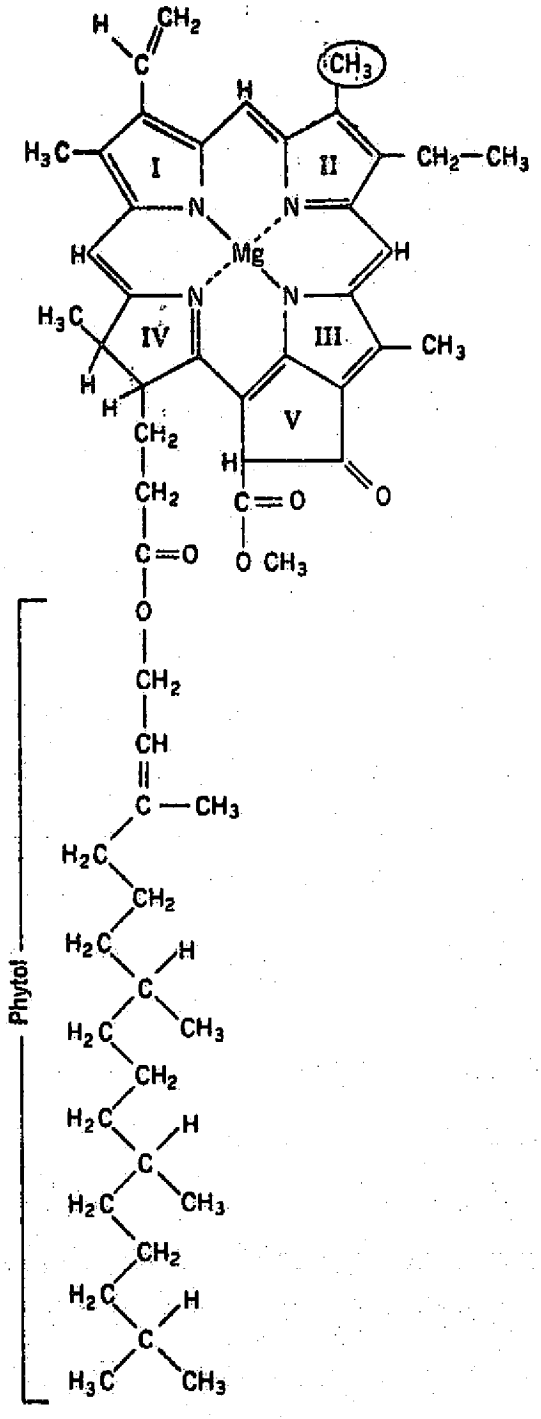

Figure 7-3. CHLOROPHYLL a

unsaturated and tends to behave as a Lewis acid (i.e., it accepts electrons from an electron donor). This is quite analogous to the strong acid catalyst properties of silica-magnesia gel in which magnesium ions are constrained by the silicate matrix to a coordination number of 4, thus generating Lewis-acid function. The electron-donor function is provided by the alicyclic ketone group ($\rangle C = O$) as a result of the fact that the energy change associated with the loss of an electron from the ketone can be delocalized and distributed over the whole porphyrin structure by resonance of the conjugated double-bond system.

As a result of its electron donor-acceptor properties, chlorophyll tends to form coordination complexes with itself and with other nucleophilic agents such as water.[30] In nonpolar solvents it exists as dimers or oligomers, the molecular weight of which is dependent on the concentration. In polar solvents, chlorophyll forms coordination adducts. Bifunctional liquids, such as dioxane and water, interact with chlorophyll to produce cross-linked coordination adducts of colloidal dimensions. Thus the structure, and therefore the properties, of Chl a will depend strongly on the chemical environment in which it exists.

On this basis, J. J. Katz and associates[30] (at Argonne National Laboratories) took a synthetic approach to delineating the nature of the antenna chlorophyll and of the reaction center. Thus the properties indicative of light harvesting and photoactivity of different synthetic chlorophyll preparations in various colloidal states and adducted with various nucleophilic agents were determined and compared with in vitro reaction-center preparations. These studies have been quite informative.

Comparative studies of the absorption spectra of the oligomers of chlorophyll in nonpolar solvents with those of in vivo reactive-center preparations provide good experimental support for the hypothesis that the bulk of the Chl a in vivo (i.e., the antenna chlorophyll) exists as high-molecular-weight oligomer (Chl a). The oligomers, however, show no indication of photoactivity, such as the photoreversible electron spin resonance signal (ESR) or the characteristic shift in absorption toward the far red (P_{700}), both characteristic of the reaction center in photosynthesis.

On the other hand, adducts with bifunctional ligands (complexing agents), such as dioxane and water, show a remarkable red shift. However, of all of the bifunctional adducts, the 1:1 chlorophyll/water adduct (Chl a·H_2O)$_n$ is the only one that shows a photoreversible ESR signal when illuminated by red light with a wavelength greater than 650 nm. These results suggest that the chlorophyll reaction center in vivo involves a nucleophilic interaction similar to the water adduct, even though the red shift in the 1:1 (Chl·H_2O)$_n$ adduct is much too large and the ESR signal much too narrow for specifically P_{700}. However, these discrepancies can be rationalized in terms of a theory that suggests the red shift and ESR signal of an isolated (Chl·H_2O·Chl) entity would be completely consistent with the in vivo P_{700}.

Thus Katz postulates a model in which one water molecule inserted into a high-molecular-weight oligomer, composed of about 300 chlorophyll molecules, is the photosynthetic unit. Mechanisms exist for a plausible explanation of the photochemical charge separation in such a model. Furthermore ESR data on P_{865} in purple photosynthetic bacteria are completely compatible with the special chlorophyll pair hypothesis.[30]

The Katz chlorophyll-pair model is also consistent with the empirical results of parallel analytical studies of the reaction center of photosynthetic bacteria. Parson and Cogdell have recently reviewed[50] the current status (as of March 1975) of understanding of the primary reactions in bacterial photosynthesis. Considerable progress has been made possible since the development of techniques (in 1968) for physically separating and purifying the reaction centers for the organism R. spheroides of light-harvesting and other components of the photosynthetic unit. These techniques led to an intensive analytical study of the nature and photochemical reactions of the reaction-center preparations.

The basic chlorophyll component of the reaction center in the bacteria R. spheroides has been shown to consist of a complex of four BChl molecules plus two molecules of BChl in which the magnesium atom has been replaced with two hydrogen atoms. ESR studies of the reaction-center preparations indicate that when the complex loses an electron, the remaining unpaired electron is shared by two of the BChl molecules, and the energy transfer with the other two BChl molecules is broken. These observations are compatible with a dual-function model such as that by Katz.[50] Furthermore, it has been

shown that dehydration (over phosphorous pentoxide) reversibly blocks the photochemical activity of bacterial chromatophores, thus implicating the water molecule as an integral part of the reaction center.

These results suggest to us that photocatalytic activity, as well as the large charge separation produced by the reaction centers, is associated with dual functionality of the reaction center. Dual functionality is inherent in the special chlorophyll pair model by Katz:

$$\text{Chl } \underline{a}\cdot H_2O\cdot\text{Chl } \underline{a} \xrightarrow{h\nu} \text{Chl } \underline{a}^{+}\cdot H_2O\cdot\text{Chl } \underline{a}^{-}$$

Such a dual-function catalyst provides for not only the generation of both an oxidant and a reductant for photocatalytic activity; but also, perhaps, double the charge separation that either half-stoichiometric, half-cell process alone could achieve.

Whether the Katz or similar models are valid remains to be demonstrated. However, the fact remains that it has been possible to synthetically prepare chlorophyll films in the laboratory that exhibit, qualitatively at least, the light harvesting and photoactive properties of the photosynthetic organisms. This accomplishment represents a large step toward synthetic photosynthesis. On the other hand, it has not yet been possible to couple the measurable photoactivity (that is, charge separation) of such chlorophyll aggregates with a suitable elelctron-transport system to achieve either chemical reaction or voltaic activity.

Primary Electron Donor and Acceptor

It is curious that the Chl^{+} generated in a methanol solution appears to be incapable of interacting with water directly. As a matter of fact, the redox potential of Chl a in methanol has been measured to be 0.62 volt,[63] clearly too weak to oxidize water (which requires 0.82 volt). Perhaps this is because the Chl^{+} ion is stabilized by forming a complex with the solvent.

The ligand effect on the stability, and therefore on the redox potential of metallic ions is a well known phenomenon. Thus the oxidation potential for the iron couple –

$$Fe^{+++} + e^{-} \rightarrow Fe^{++}$$

varies from as high as 1.14 volts (with electron-withdrawing ligands such as

1, 10 phenanthroline) to 0.36 volt (with anionic electron-donor ligands such as cyanide ion, CN^-). The standard oxidation potential for Fe^{+++} in which the ligand is water is 0.77 volt.[2] It is also very interesting that the oxidation potential of Fe^{+++} is reduced even further in the electron-transport enzymes – for example, to a range of from –0.3 to +0.3 volt in cytochromes and to only –0.42 volt in ferredoxin.

Thus the ligand environment of the oxidant and reductant produced by the photocatalyzed reaction may be critical in determining the charge separation attained and the reactivity of the species. On this basis, the function of the electron-donor and -acceptor molecules immediately associated with the photocatalyst may be to provide the ideal ligand field for the terminal oxidant and reductant, thus facilitating electron transport and reaction with water.

Support for such an effect is cited in the Parson and Cogdell review[50]:

> "The E_m values that have been reported for P_{870} are significantly below that of bacteriochlorophyll in solution, which is +0.52 volt in methanol and +0.64 volt in CH_2Cl_2.... The E_m of chlorophyll in alcoholic solution varied by 0.23 volt, in the series methanol < ethanol < i-propanol. Although the effect awaits rationalization, it could reflect the complexing of the alcohol with the chlorophyll Mg atom or with the ring keto oxygen."

On the other hand, an equally important property of the primary electron acceptor is to quench the fluorescence of the excited chlorophyll (i.e., to trap the electronic energy). Parson and Cogdell cite[50] literature indicating that the quenching ability of electron acceptors decreases with decreasing redox potential (i.e., the better the oxidant, the greater the quenching ability). On the other hand, the quench rates increase with increasing concentration, up to the point at which diffusion becomes controlling. Such factors probably, in part, account for the fact that photochemical reactions in solution do not seem to bridge a large energy gap.

Recent studies of reaction-center preparations from bacteria (as interpreted by Parson and Cogdell) also indicate that the primary electron acceptor of the photochemical process is an integral component of the reaction center. Its composition is still unknown; but both a quinone and an iron-containing complex (probably similar to ferredoxin) are involved in series, in parallel, or as an integral complex. The intimate relationship (analogous to infinite

concentration with no diffusion control) probably permits use of the acceptor with the lowest oxidation potential (i.e., with the highest reduction potential) without a reduction in the trapping efficiency.

In addition to four BChl molecules and the iron and quinone species, the reaction-center complex contains three protein components of differing molecular weight in a mole ratio of 1:1:1. These proteins undoubtedly have an important function in binding the components together and in providing the ideal ligand environment. For example, denaturation of the protein results in a drastic shift of the adsorption spectrum from that characteristic of the reaction center (with the major peak at 870 nm) to that of monomeric BChl in solution (with the major peak at 760 nm).[14,15,52] Because the heavier unpigmented fraction can be physically removed (by detergent treatment) without affecting the photoactivity, the photochemical activity apparently resides in the two lower molecular weight fractions.[23,38,63]

Considerable information has also been gathered on the kinetics of the photochemical events occurring in the reaction center in terms of rates of absorption, fluorescence, and charge separation (ESR). In this way, the structural and functional relationships are gradually being elucidated, although no quantitative mechanism has yet emerged. The reaction center is apparently a dual function photosensitizer (e.g., Chl·H_2O·Chl), the photocatalytic activity of which depends on an intimate relationship or complexing with an electron acceptor to trap the photonic energy that would otherwise be reemitted as fluorescence. The primary electron donor appears to be less strongly bound to the reaction center, but in reality it is probably also an integral component of this reaction center. Its role in quenching fluorescence has not been identified, but it is nevertheless required to transmit the positive charge to a reactant. The redox potentials of the donor and acceptor species are dependent on the nature of the ligands provided and seem to be tailored to achieve maximum charge separation, as well as the specific potential levels required to oxidize water in PS II and to reduce NADP in PS I.

This understanding of the reaction center and the empirical observations of the complex structure involved suggest that the laboratory synthesis of photocatalytic membranes, complete with electron transport, will require a major breakthrough. However, the knowledge gained thus far does indicate the direction for further research.

Nonbiological Photolysis

The energy of the carbon-oxygen single bond is about 111 kcal/mole, equivalent to the energy of UV light that has a wavelength of about 260 nm. Furthermore, water does not absorb UV light at wavelengths greater than 185 nm (equivalent to an energy of 155 kcal/Einstein). Obviously, direct photolysis is not possible with sunlight, which does not contain UV light below about 300 nm.

On the other hand, we have learned from photosynthesis that photolysis of water can be carried out by red light that has an energy content of only 40 kcal/Einstein if the energy is applied incrementally to one electron at a time. This is analogous to the electrolysis of water, which can be driven by energy units as small as 28.4 kcal/Einstein (1.23 volts). Thus the low energy content of the available solar radiation does not preclude the possibility of developing a relatively efficient photolysis process. It does, however, impose rather severe constraints on how such a process can be accomplished.

It has been estimated that the theoretical maximum free energy (ΔG_{max}) made available by absorption of light is limited by the second law of thermodynamics to about 70% of the energy of the light absorbed.[31] Thus red light at 700 nm, which has an energy content of 1.8 volts, theoretically can provide a net free energy of 1.26 volts (1.8 X 0.7), which is sufficient to drive the splitting of water. However, in photosynthesis, 700-nm light yields a charge separation of only about 1 volt (an overall efficiency of 55%). On the basis of a 55% efficiency, the photogeneration of 1.23 volts would require quantum energy of 2.24 volts (~543-nm light). If 1.47 volts (corresponding to the reaction enthalpy) is actually required to electrolyze water, a quantum energy of 2.7 volts (~450-nm light) would be required. Thus it seems improbable that direct, one-step photolysis or electrolysis of water can be accomplished, except at short wavelengths.

Requirements for Efficient Photolysis by Sunlight

Because water does not absorb visible light, attainment of efficient photochemical reaction will require special considerations:

- For efficient utilization of the solar flux, a sensitizer must be used that is capable of utilizing all or a substantial part of the visible spectrum. Most pure chemicals absorb over a fairly narrow portion of the visible spectrum. Thus it may be necessary to employ one or more accessory pigments for harvesting light. This, in turn, would require a mechanism for efficient transfer of harvested energy to the sensitizer. These requirements suggest that perhaps a black pigment (e.g., a carbon or graphite) should be considered. However, the best possibility seems to be the oligomeric Chl a membranes described by Katz.[30]

- The photochemical reaction must be photocatalytic or capable of coupling to other reactions to close the cycle. Generally, photochemical reactions are stoichiometric and result in the oxidation or reduction of the sensitizer. Such reactions comprise only one half-cell reaction of a photocatalytic reaction. Therefore, the sensitizer in its altered oxidation state must be capable of driving a second half-cell reaction, either in situ or in a separate stage, to regenerate the original sensitizer and to complete the desired reaction.

- Electron-transport mechanisms will be required to couple the sensitizer to the reaction system or to couple one half-cell reaction to the other. Thermodynamic considerations suggest that at least two photocatalytic reactions will be required analogous to the requirement of 2 quanta per electron for photosynthesis. Therefore, means must also be provided for coupling two or more reactions into a complete system that produces hydrogen and oxygen from water. Conversely, thermodynamic considerations limit the number of photocatalytic reactions that can be used in series efficiently. For example, if photosynthesis required 4 quanta per electron instead of two, the maximum efficiency would be halved.

These criteria obviously have been set up by analogy with photosynthesis, which is the only model we have to work from at present. From this point of view, it might also be useful to set up an idealized process analog of photosynthetic hydrogen production as a working model. Such a model would consist of three discrete reaction stages that operated in sequence (in series) to split water as follows:

$$2H_2O + 2Q \xrightarrow[\text{PS II}]{h\nu} O_2 + 2QH_2 \qquad (1)\ E_1 \approx 1$$

$$2QH_2 + 2P \longrightarrow 2Q + 2PH_2 \qquad (2)\ E_2 \approx -0.8$$

$$2PH_2 \xrightarrow[\text{PS I}]{h\nu} 2P + 2H_2 \qquad (3)\ E_3 \approx 1$$

$$2H_2O \xrightarrow[\text{PS I + II}]{h\nu} O_2 + 2H_2 \qquad E \approx 1.23$$

The light-driven reactions, 1 and 3, require quantum energies equivalent to about 1 volt and are coupled through Reaction 2, which occurs spontaneously with the release of energy. Thus the photosynthetic model suggests that to accomplish the overall reaction in three stages with only light-driven reactions, it is necessary for each photochemical event to involve water directly — one producing oxygen, and the other producing hydrogen. Futhermore, each light-driven reaction must achieve a net energy input equivalent to more than 0.6 volt so that Reaction 2 occurs spontaneously. Otherwise a portion of the hydrogen produced must be used to drive Reaction 2. However, it is possible to achieve a completely light-driven cycle with only two photochemical steps without direct involvement of water if the energy gap bridged is sufficient to generate products from which hydrogen and oxygen can be recovered by spontaneous reactions. This would, however, require additional reaction stages.

Photochemical Sensitizers

It is not surprising that natural evolutionary processes resulted in as complex a photocatalyst as chlorophyll: It is difficult to find simple photosensitizers that can utilize visible light and that are capable of interacting with water. Most inorganic materials that can photooxidize or reduce water do so only in the UV-light range and can therefore utilize only a small fraction of the light in the visible range. Such materials, therefore, are not suitable for efficient solar photolysis. Examples of such reactions with inorganic materials include —

$$2Ce^{++++} + H_2O \rightarrow 2Ce^{+++} + 1/2O_2 \quad ^{27}$$

$$Fe^{++} / H^{+} \rightarrow Fe^{+++} + 1/2H_2 \quad ^{28}$$

$$Cr^{++} + H^{+} \rightarrow Cr^{+++} + 1/2H_2 \quad ^{17}$$

The first of these reactions (i.e., the ceric-ion oxidation of water) does not even represent a storage of solar energy because the ΔG_{298} for the reaction is negative.

The basic problem appears to be that most inorganic materials are weakly absorptive of light in the visible range, and those that are colored yield excited states (or ions) that are not capable of reacting with water. Most colored ions are ions of the transition metals. According to Basolo and Pearson, [2] most ionic complexes of the transition metals exhibit two distinct types of

light absorption. Absorption of visible light is of low intensity and produces electronic transitions that lead not to charge transfer, but only to weakening of the ligand bonding. Such effects can promote reactions such as ligand substitution and racemization, but not oxidation-reduction reactions. The intense absorption in the ultraviolet region is of the "charge-transfer" type and is "characteristic of associated pairs of molecules, where we can identify a charge donating group and a charge accepting group, or alternatively, a Lewis base and a Lewis acid, or a reductant and an oxidant." Absorption of light in the visible range involves primarily d-orbital electrons, and "The intensity is low because the transitions are parity forbidden and sometimes spin forbidden."[12]

On the other hand, a number of highly colored organic materials are known, many of which do undergo photochemical oxidation-reduction reactions under the influence of visible light[52]:

$$\text{dye} + 2Fe^{++} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} \text{leucodye} + 2Fe^{++}$$

However, the reactions thus far discovered result in the generation of relatively small EMF's (from 0.2 to 0.3 volt), and none generate an oxidant or reductant strong enought to react with water. Such reactions are stoichiometric. However, if the reaction is carried out in an emulsion of ether in water, the product leucodye can be continuously extracted, thus resulting in the storage of solar energy in the form of a leucodye.[52]

Thus far, our experience suggests that the probability of finding a simple inorganic or organic photosensitizer is not great. However, it should be emphasized that investigation of the photochemical properties of materials absorbing light in the visible range has not been extensive. Thus the field is wide open for research, particularly because we know photochemical water splitting can be done (i.e., as in photosynthesis). At present, the Katz approach[30] seems to have the greatest potential.

Summary and Conclusions

Photosynthesis in green plants is a process that results ultimately in the splitting of water into molecular oxygen and a strong reducing species with an electrochemical potential below that of hydrogen. Thus the photosynthetic

process is thermodynamically capable of producing hydrogen and oxygen from water. However, it appears to be universally true that, in green plants, the reducing power so generated is always used for the reduction of carbon dioxide to carbohydrate and other cell material.

Certain bacteria and algae do contain enzymes, such as hydrogenase and nitrogenase, that are capable of catalyzing the reduction of hydrogen ions to molecular hydrogen. Such organisms do in fact produce hydrogen under certain conditions by photochemical and dark reactions. However, this hydrogen is not produced from water, but is produced at the expense of an energy-rich nutrient substrate supplied by a separate photosynthetic process (performed by either itself or other organisms). Thus the two biological mechanisms required for producing hydrogen and oxygen from water exist in nature in separate organisms. The questions then become whether and how efficiently the two functions can be coupled to split water directly.

Obviously, it is possible to produce hydrogen and oxygen from water by a conventional two-stage process with living and growing organisms — that is, by the conversion of photosynthetic marine or agricultural residues to hydrogen by anaerobic fermentation or by the action of photosynthetic bacteria. Such processes have been proposed, and hydrogen production by fermentation with clostridial species actually has been performed commercially. However, hydrogen is produced in such processes only as a by-product of the primary production of alcohols, ketones, or fatty acids. Presumably, better strains could be developed to maximize hydrogen production. However, there may be a basic limitation in the efficiency (or kinetics) because biological hydrogen production appears to have a regulatory function, rather than a metabolic function by which organisms can live and grow. Such processes would merely represent alternative methods for converting primary photosynthetic products to useful fuels, such as methane and alcohol, which are much closer to commercial feasibility.

We do not discount the potential for hydrogen or methane production from carbonaceous photosynthetic residues, particularly those that would otherwise be waste materials (i.e., sewage or garbage). However, they are ultimately subject to the basic limitation in the efficiency at which solar energy can be converted in marine and agricultural residues to feedstock for hydrogen or methane production.

A number of other biological approaches have been suggested for the production of hydrogen:

a. Genetic improvement of certain nitrogen-fixing algae species in which the biological functions for both water splitting and ammonia or hydrogen production do coexist, but in separate cells. In the absence of nitrogen gas and with the proper nitrogenous nutrients supplied, such species do, in fact, produce hydrogen and oxygen from water. However, the solar-utilization efficiencies are significantly lower than in normal photosynthesis.

b. Direct coupling of bacterial hydrogenase with the intact photosynthetic apparatus extracted from algae or green plants. The scientific feasibility of this approach has been demonstrated (in μmole quantities) in the laboratory. However, two substantial problems remain: The hydrogenase activity is destroyed by oxygen, and the catalyst life of the intact photosynthetic apparatus in vitro is very short (lasting only minutes).

c. Two-stage coupling in which the aerobic and anaerobic functions are separated processwise. In the first stage, water splitting is performed, producing a stable reductant other than carbohydrate, by the intact photosynthetic apparatus extracted from algae. The stable reductant is then separated and reacted with hydrogenase in a second stage. The scientific feasibility has been demonstrated (in μmole quantities) in the laboratory with a fairly complex biological chemical. Obviously, a simpler stable reductant is needed; and the brevity of the catalyst life remains the primary problem.

The above approaches are all based on utilization of the intact photosynthetic apparatus of natural organisms. However, when removed from the self-repairing environment of the living organism, the photocatalytic life of these complex systems tends to be very short. Although some progress has been made toward stabilization or protection of these systems, a major research effort will be required before successful application can be expected.

Significant progress toward synthetic photosynthesis has been made by development of synthetic chlorophyll membranes that exhibit, at least qualitatively, the light-harvesting capability and photoactivity of photosynthetic membranes. However, it has not been possible to couple such membranes to the electron-transport mechanism required to achieve photochemical or photovoltaic action. Furthermore, a major breakthrough may be required before this coupling can be achieved.

The major barrier to understanding how the primary photosensitizing entity is coupled to electron transport has been the lack of effective analytical tools. It is our impression that the barrier is beginning to yield to a combination of analytical, synthetic, and theoretical approaches; however, the breakthrough may still be a few years hence.

There can be little doubt that photosynthesis has vast potential for converting solar energy to chemical energy for use as fuel, as well as food:

- Theoretically, the photosynthesis process is capable of converting up to 10% of the solar flux to chemical energy.
- Under laboratory conditions, efficiencies approaching 10% have been observed with algae.
- Maximum daily efficiencies as high as from 5% to 6% have been achieved in agriculture.
- If the theoretical maximum efficiency of 10% based on total solar flux could be achieved, production from about 1% of the total area of the United States would be sufficient to meet all of our energy needs.

The maximum annual marine or agricultural efficiency achieved is about 3%, but efficiencies are usually much lower — in the range of from 0.5% to 1.5% conversion of the total solar flux. It becomes evident, therefore, that the primary goal should be to increase the efficiency of oxygen generation by the basic process; and whether the reducing is utilized to produce hydrogen directly or to produce other reduced materials, such as carbohydrate, methane, or ammonia, should be of secondary import.

On the basis of current knowledge, nonbiological photolysis does not appear promising. However, investigation of the potential of this approach has not been extensive, and the field is wide open for research. It is our feeling that exploratory synthetic work in this area, guided by parallel research on the mechanisms of photosynthesis, will prove worthwhile.

In conclusion, there is no doubt that photosynthesis offers a vast potential for the production of energy, as well as of food and organic materials. It is also clear that the great challenge to research in this area is increasing the rate of transduction of solar energy to chemical energy, whether as food or as fuel. Although first priorities are, and should be, directed toward food production, in the long run it makes little difference because food and energy are, to a major extent, interconvertible. Furthermore, it

is conceivable that higher efficiencies of solar-energy conversion can be achieved by engineered "in vitro" photosynthetic processes than by conventional marine or agricultural processes, particularly on an annual basis.

References Cited in This Section

1. Arnon, D. I., Mitsui, A. and Paneque, A., "Photoproduction of Hydrogen Gas Coupled With Photosynthetic Phosphorylation," Science 134, 1425 (1961).

2. Basolo, F. and Pearson, R. G., Mechanisms of Inorganic Reactions, Second Ed. New York: John Wiley and Sons, 1958.

3. Beesch, S. C., "Acetone-Butanol Fermentation of Sugars," Ind. Eng. Chem. 44, 1677-682 (1952).

4. Benemann, J. R., Berenson, J. A., Kaplan, N.O. and Kamen, M. D., "Hydrogen Evolution by a Chloroplast-Ferredoxin-Hydrogenase System," in Proc. Nat. Acad. Sci. USA 70, No. 8, 2317-320 (1973) August.

5. Benemann, J. R. and Weare, N. M., "Hydrogen Evolution by Nitrogen-Fixing Anabaena cylindrica Cultures," Science 184, 174-75 (1974) April 12.

6. "Bioconversion," Hearings Before the Subcommittee on Science and Astronautics, U.S. House of Representatives, No. 40. Washington, D.C.: U.S. Government Printing Office, 1974.

7. Bishop, N. I., "Photo-Hydrogen Metabolism in Algae: Can This Process Be Utilized and an Energy Produced of Any Magnitude?" in Proc. Workshop Bio-Solar Energy Convers. 9-13 (1973) September.

8. Blankenship, D. T. and Winget, G. D., "Hydrogen Fuel: Production by Bioconversion," in Intersoc. Energy Convers. Eng. Conf. Eighth Proc. 580-82. New York: AIAA, 1973.

9. Brown, A. H., "Bioconversion of Solar Energy," Chem. Technol., 434-37 (1975) July.

10. Calvin, M., "Solar Energy by Photosynthesis," Science 184, 375-81 (1974) April 19.

11. Carlson, P. S. and Polacco, J. C., "Plant Cell Cultures: Genetic Aspects of Crop Improvement," Science 188, 622-25 (1975) May 9.

12. Chedd, G., "Cellulose From Sunlight," New Sci., 572-75 (1975) March 6.

13. Cheniae, G. M., "Photosystem II and Oxygen Evolution," Annu. Rev. Plant Physiol. 21, 467-98 (1970).

14. Clayton, R. K., Molecular Physics in Photosynthesis. New York: Blaisdell Publishing Co., Inc., 1965.

15. Clayton, R. K., Light and Living Matter: a Guide to the Study of Photobiology, Vol. 2. New York: McGraw-Hill Book Co., 1971.

16. Clayton, R. K., "Physical Mechanisms in Photosynthesis: Test Elucidations and Current Problems," in Proc. Nat. Acad. Sci. USA 69, No. 1, 44-49 (1972) January.

17. Collinson, E., Dainton, F. S. and Malati, M. A., "The Photooxidation of Chromous Ions in Aqueous Solution at 25°C," Trans. Faraday Soc. 55, 2096 (1959).

18. Fujishima, A. and Honda, K., "Electrochemical Photolysis of Water at a Semiconductor Electrode," Nature 238, 37 (1972).

19. Gaffron, H. and Rubin, J., "Fermentative and Photochemical Production of Hydrogen in Algae," J. Gen. Physiol. 26, 219-40 (1942).

20. Gibbs, M. et al., "Summary Statement," in Proc. Workshop Bio-Solar Energy Convers. 1-6 (1973) September.

21. Goodwin, T. W., Ed., Chemistry and Biochemistry of Plant Pigments. New York: Academic Press, 1965.

22. Govindjee, Ed. Bioenergetics of Photosynthesis. New York: Academic Press, 1975.

23. Govindjee and Govindjee, R., "The Absorption of Light in Photosynthesis," Sci. Am. 231, No. 6, 68-81 (1974) December.

24. Graves, D. J. and Stramondo, J. G., "Photosynthesis as a Model for Photochemical Hydrogen Generation." Paper No. 9 presented at the Symposium on Energy From Biological Conversion (Practice), 79th International A.I.Ch.E. Meeting, Houston, March 17-19, 1975.

25. Gray, C. T. and Gest, H., "Biological Formation of Molecular Hydrogen," Science 148, 186-92 (1965) April 9.

26. Hardy, R. W. F. and Havelka, U. D., "Nitrogen Fixation Research: a Key to World Food?" Science 188, 633-43 (1975) May 5.

27. Heidt, L. J. and McMillan, A. F., "Conversion of Sunlight Into Chemical Energy Available in Storage for Man's Use," Science 117. 75-76 (1953).

28. Heidt, L. J. et al., "Gross and Net Quantum Yields at 2537 Å for Ferrous to Ferric in Aqueous Sulfuric Acid Solution and the Accompanying Reduction of Water to Gaseous Hydrogen," J. Phys. Chem. 66, 336 (1962).

29. Kaplan, N. O. et al., "Studies on Purified Bacterial Hydrogenase and Its Use in Energy Production." Paper presented at the Symposium on Unusual Fuels Production, Division of Fuel Chemistry, American Chemical Society, Philadelphia, April 6-11, 1975.

30. Katz. J. J. and Norris, J. R., "Chlorophyll and Light Energy Transduction in Photosynthesis," Current Topics in Bioenergetics, Vol. 5, 41-75. New York: Academic Press, 1973.

31. Knox, R. S., "Thermodynamics and the Primary Process of Photosynthesis," Biophys. J. 9, 1351-362 (1969).

32. Kok, B., "Efficiency of Photosynthesis," in San Pietro, A. and Gest, H., Eds., Horizons of Bioenergetics. New York: Academic Press, 1972.

33. Kok, B., "Photosynthesis," in Proc. Workshop Bio-Solar Energy Convers., 22-30 (1973) September.

34. Krampitz, L. O., "Hydrogen Production by Photosynthesis and Hydrogenase Activity – an Energy Source," Rep. No. NSF/RA/N-73-017, prepared by Case Western Reserve University, Cleveland, August 1973.

35. Krampitz, L. O., Case Western Reserve University, private communication of February 6, 1975.

36. Krampitz, L. O., "Biophotolysis of Water to Hydrogen and Oxygen." Paper presented at the Symposium on Unusual Fuels Production, Division of Fuel Chemistry, American Chemical Society, Philadelphia, April 6-11, 1975.

37. Krasnovsky, A. A., "The Models of the Evolution of Photochemical Electron Transfer," in Buvet, R. and Ponnamperuma, C., Eds., Chemical Evolution and the Origin of Life. Amsterdam: North-Holland Publishing Co., 1971.

38. Lehninger, A. L., Bioenergetics. The Molecular Basic of Biological Energy Transformations, Second Ed. Menlo Park, Calif.: W. A. Benjamin Inc., 1971.

39. Loomis, R. J., Williams, W. A. and Hall, A. E., "Agricultural Productivity," Annu. Rev. Plant Physiol. 22, 431-68 (1971).

40. Marx, J. L., "Nitrogen Fixation: Research Efforts Intensify," Science 185, 132-36 (1974) July 12.

41. Mitchell, P., "Coupling of Phosphorylation to Electron and Hydrogen Transfer by a Chemi-osmotic Type of Mechanism," Nature 144, 144-48 (1961) July 8.

42. Mitsui, A., "The Utilization of Solar Energy for Hydrogen Production by Cell-Free System of Photosynthetic Organisms." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami, March 1974.

43. Mitsui, A., "Photoproduction of Hydrogen via Microbial and Biochemical Processes," in Veziroglu, T. N., Ed., Hydrogen Energy Fundamentals, Miami Beach, March 3-5, 1975.

44. Monty, K. J. and Beck, R. W., "The Genetic Reengineering of Photosynthetic Microorganisms to Obtain Efficient Hydrogen-Producing Photosystems," in Proc. Workshop Bio-Solar Energy Convers., (1973) September.

45. National Science Foundation, An Inquiry Into Biological Conversion — a Workshop Report. Gatlinburg, Tenn., 1972.

46. National Science Foundation, Proc. Workshop Bio-Solar Energy Convers., (1973) September.

47. "Newsletter," Adv. Battery Technol. 11, No. 6, 3 (1975) June.

48. Ohta, T. and Kimaya, M., "Photochemical Splitting of Water by Solar Energy," in Proc. Ninth Intersoc. Energy Convers. Eng. Conf., 317 (1974).

49. Packer, L., Murakami, S. and Mehard, C. W., "Ion Transport in Chloroplasts and Plant Mitochondria," Annu. Rev. Plant Physiol. 21, 271-304 (1970).

50. Parson, W. W. and Cogdell, R. J., "The Primary Photochemical Reaction of Bacterial Photosynthesis," Biochim. Biophys. Acta 416, 105-49 (1975).

51. Peters, G. A. and Mayne, B. C., "The Azolla-Anabaena Azollae Relationship: I. Initial Characterization of the Association," Plant Physiol. 53, 813-19 (1974); "II. Localization of Nitrogenase Activity as Assayed by Acetylene Reduction," ibid., 820-24 (1974).

52. Rabinowitch, E. and Govindjee, Photosynthesis. New York: John Wiley and Sons, 1969.

53. Racker, E. and Stoeckenius, W., "Reconstruction of Purple Membrane Vesicles Catalyzing Light-Driven Proton Uptake and Adenosine Triphosphate Formation," J. Biol. Chem. 249, 662-63 (1974).

54. Reid, R. and Leese, H., "A New Form of Biological Power," New Sci. 65, 310 (1975) February 6.

55. San Pietro, A. and Gest. H., Eds., Horizons of Bioenergetics. New York: Academic Press, 1972.

56. Schneider, T. R., "Efficiency of Photosynthesis as a Solar Energy Converter," Energy Convers. 13, 77-85 (1973).

57. Schwartz, M., "The Relation of Ion Transport to Phosphorylation," Annu. Rev. Plant Physiol. 22, 469-84 (1971).

58. Shanmugum, K. T. and Valentine, R. C., "Molecular Biology of Nitrogen Fixation," Science 187, 919-24 (1975) March 14.

59. Stuart, T. S., "Nature of the Desired Reduced Product in Bio-Solar Energy Processes," in Proc. Workshop Bio-Solar Energy Convers., 45-55 (1973) September.

60. Surzycki, S. J., "Biological Energy Conversion: Genetic Feasibility," in Proc. Workshop Bio-Solar Energy Convers., (1973) September.

61. Szego, G. C. and Kemp, C. C., "Energy Forests and Fuel Plantations," Chem. Technol., 275-84 (1973) May.

62. Togasaki, R. K., "A Proposal to Search for Mutant Strains Carrying Oxygen-Resistant Hydrogenase," in Proc. Workshop Bio-Solar Energy Convers., (1973) September.

63. Vernon, L. P. and Seely, G. R., The Chlorophylls. New York: Academic Press, 1966.

64. Zelitch, I., "Improving the Efficiency of Photosynthesis," Science 188, 626-33 (1975) May 9.

65. Zumft, W. G. and Mortenson, L. E., "The Nitrogen-Fixing Complex of Bacteria," Biochim. Biophys. Acta 416, 1-52 (1975).

8. HYDROGEN PRODUCTION BY OTHER PROCESSES — J. B. Pangborn and D. P. Gregory

In addition to the hydrogen production processes that have been described in earlier sections, there are three more processes that, although not mentioned as often as the others in connection with the large-scale use of hydrogen, deserve some attention. One of these is the production of hydrogen from waste materials, such as sewage, garbage, and agricultural wastes. Another is the splitting of water through use of neutron or ultraviolet radiation in a chemical sequence resembling a thermochemical process. The last process, the direct thermal dissociation of water, deserves special attention because it could make use of solar energy.

Hydrogen Production From Waste Materials

There is a possibility that hydrogen can be produced from waste materials such as sewage, garbage, and agricultural wastes. These materials, largely cellulosic, represent a considerable reserve of "energy" and are currently being considered as feedstocks for a variety of synthetic fuel production processes. Hydrogen production must be considered as a possible option.

Cellulosic wastes can be converted to a variety of fuels by four primary routes: 1) partial oxidation, 2) high-temperature reaction with steam, 3) pyrolysis, and 4) fermentation. In the first three cases, the initial process is one of gasification, converting the cellulosic material to a raw gas that consists primarily of hydrogen, carbon monoxide, carbon dioxide, and hydrocarbons, together with many other components. This gas stream can then be processed in a variety of ways to yield methane, methanol, synthetic "gasoline," or hydrogen, or it can be used directly as a boiler fuel. In the fourth case, depending on the selected fermentation agent and fermentation conditions, a variety of products can be derived, including alcohols, methane, or hydrogen.

Considerable research is already under way for the development of commercially viable processes, employing each of the methods described above, for the production of SNG (primarily methane), liquid hydrocarbons, and alcohols from sewage, garbage, and agricultural wastes. There seems to be little or no effort directed toward the production of hydrogen. However, the problems being addressed are primarily concerned with the initial conversion

of the raw waste to "raw gas" and are those that result from the considerable variation in feedstock "quality," which in turn results in much variation in the raw-gas composition. For this reason, most processes entering the commercial-application stage are those in which the raw gas is simply used as a boiler fuel, often added to a conventional fuel supply such as coal, oil, or natural gas.

Once consistent raw-gas production has been achieved there seems to be little doubt that a fairly conventional gas "clean-up" process could be designed to produce hydrogen-rich gas rather than SNG or a liquid fuel, should the need exist. Therefore, there seems to be little justification at this stage for setting up a special research program aimed at producing pure hydrogen from these waste-material feedstocks. In the case of fermentation processes, the problems are similar to those already described in the section on photosynthetic hydrogen production.

A word of caution is appropriate at this point. There will be continuing demand for hydrocarbons and carbon-based organic materials long after conventional sources of fossil fuels have been depleted. Because the waste materials considered here are all carbonaceous, they must be regarded as an important source of organic carbon for such applications as lubricants, plastics, and pharmaceuticals. In the long run, it may be quite wrong to consider using them as a source of hydrogen and to develop processes that break down the organic carbon molecules.

Hydrogen Production by Radiation

Researchers at KMS Fusion, Inc., a private company in Ann Arbor, Michigan, have been carrying out research on the production of fusion energy through use of a laser beam. They have achieved significant success in producing fusion reactions by irradiating deuterium-tritium targets with laser energy, and the resulting fusion reaction produces a burst of radiation that consists primarily of neutrons with an energy of 14 MeV. They are still trying to demonstrate the "break-even point," at which their equipment will produce as much energy as it consumes. In parallel with this work is a project, funded by Texas Gas Transmission Corp., for the development of a process that splits water into hydrogen and oxygen under the influence of 14-MeV neutron irradiation. Thus, the successful development of such a process would enable hydrogen to be produced from a nuclear fusion reactor without the intermediate production of electricity and heat.

Details of the hydrogen-generation process have not been released, and staff at both KMS Fusion and Texas Gas Transmission Corp. regard this work as highly proprietary. However, representatives of KMS have announced[2] that they are actually producing hydrogen in the laboratory through a process that is driven by 14-MeV neutrons, that are obtained from a cyclotron. They describe the process as being similar to a thermochemical reaction sequence, in which a number of chemical processes are carried out in a cyclic fashion, but the energy supply to this sequence comes from one or more steps that absorb neutron energy rather than absorbing heat.[7] They point out that such a process offers considerable advantage over thermochemical processes because it is not necessary to include a high-temperature step; thus corrosion of process equipment is less likely to occur. Because no experimental results have been released, it is impossible to assess the status of this research; but it was recently announced that Texas Gas Transmission Corp. has renewed its funding of KMS's program for a second year at a very substantial level, which gives credence to the belief that significant progress is being made. To our knowledge, no other company is investigating similar processes.

Chemonuclear Water Splitting

In fusion reactions, deuterium nuclei are combined to form helium nuclei (alphas). In fission reactions, U^{235}, U^{233}, Pu^{239}, etc., are split into fission fragments whose kinetic energy represents about 85% of the energy released by the fission process. Use of the high-energy radiation from nuclear fusion or use of the kinetic-energy fission products to excite or ionize molecules and to break chemical bonds has been suggested by Juppe[9] and by Harteck and Dondes[8] as a means for the production of hydrogen from water. Experiments have shown that water can be split with fission fragments and that steam can be split with alpha irradiation.

IGT has been granted a patent on a multistep thermochemical process in which the chemonuclear decomposition of carbon dioxide to carbon monoxide and oxygen is used.[14] In this process, invented by C. G. von Fredersdorff, hydrogen is produced thermochemically by the action of steam on iron, and the iron oxide so produced is reduced with carbon monoxide to carbon dioxide. Fissiochemical decomposition of the carbon dioxide, by exposure to high-velocity fission fragments, reproduces the

carbon monoxide and liberates oxygen. In principle, fissiochemical reactions are different from thermochemical or direct (single-step) thermal water-splitting steps, which could use the heat generated by a nuclear reactor. (In conventional nuclear reactors, the fission products are slowed by collisions to yield their energy as heat.)

For hydrogen and oxygen production from water via chemonuclear splitting, efficiency is measured in terms of the number of water molecules split per dose of radiation (100 eV by convention). The enthalpy required to split liquid water, 68,300 cal/g-mol, corresponds ideally to 33.8 molecules of hydrogen produced/100 eV; and the enthalpy required to split steam, 57,900 cal/g-mol, corresponds ideally to 39.9 molecules of hydrogen produced/100 eV. For fission-fragment bombardment of water, an experimental chemonuclear yield of 1.75 splits/100 eV has been reported; this corresponds to an efficiency of 5%. For alpha irradiation of steam, a yield of 6 splits/100 eV has been observed; this corresponds to an efficiency of 15%.[9] The use of fusion reactors to produce hydrogen from steam is a technology that may be developed in 30 to 50 years. The experimental verification of a self-sustaining fusion reaction is yet to be demonstrated, and a commercial fusion technology must be considered speculative at this date.

Although fission reactors are in commercial use today, a configuration for chemonuclear reactions is not practical because of the requirements for containment of radioactive material. That is, fission products must be contained by the fuel particles in the reactor core. A fission reactor for chemonuclear-reaction use would then need a thin, high-surface-area nuclear fuel structure through which the chemical reactants could pass to be exposed to fission-fragment tracks. In gaseous systems, this track is about 2 centimeters long; and in condensed systems, it is on the order of 20 microns long. Honeycomb fuel foil structures have been fabricated to make about 38% of the fission-fragment energy available for chemonuclear reactions. The main technical problem with this configuration is that the chemical reactant streams become contaminated with all manner of fission-product radioactivity.

Nuclear-Photochemical Water Splitting

Water can be split into hydrogen and oxygen by exposure to ultraviolet (UV) light of the correct wavelength; however, a spectrum of UV light will produce many excited states and radicals that are not desired. Water is transparent to visible light, but wavelengths of less than 2000 Å are absorbed. A continuum from about 1850 to about 1450 Å results in —

$$H_2O \rightarrow H + OH \qquad (8\text{-}1)$$

With UV light at 1849 Å, Ung and Back[13] observed the production of hydrogen and hydrogen peroxide from steam at 200 °to 350 °C. In the vicinity of 1236 Å, another decomposition mechanism has been observed:

$$H_2O \rightarrow H_2 + O \qquad (8\text{-}2)$$

For this mechanism, nearly monochromatic or quite-intense, narrow-spectrum UV light would be required for significant yields of hydrogen, and the light would have to be produced artificially. Only insignificant intensities of sunlight at these wavelengths reach the earth's surface.

Eastlund and Gough[4] have proposed the use of a "fusion torch" for producing UV light for water splitting. They conclude that because water molecules, under bombardment by the ultraviolet rays of sunlight, are split apart (producing hydrogen and oxygen) in the upper atmosphere, the same process might be achieved on the earth's surface by using radiation from controlled fusion. They have calculated the requirements for a photolysis system, including a fusion reactor that generates plasma energy and a plasma-leakage stream that produces the correct UV light for transmission through a window (of unspecified character) and into water vapor. By using an optimistic plasma energy-to-photon conversion, a hydrogen production efficiency of about 20% is achieved. Waste energy is converted to electricity and then to hydrogen by electrolysis for an overall system efficiency (UV light to hydrogen) of 36%. Based on the reactor plasma energy, the system efficiency is about 29%.

Photolysis can be combined with other mechanisms to split water and produce hydrogen. For example, in an aqueous solution (or vapor) of mercury atoms, the photosensitized decomposition of water by excited mercury atoms occurs; mercuric oxide is produced, and hydrogen is evolved. The quantum yield (water molecules split per photon) is about 0.02 at

1849 Å.[11] Temperatures of 500° to 700° C are adequate for decomposing the mercuric oxide to mercury and oxygen, thus closing the cycle.

Direct Thermal Decomposition of Water to Produce Hydrogen

Description of the Direct Decomposition Reaction

At sufficiently high temperatures, water (steam) will undergo appreciable dissociation into its elements, hydrogen and oxygen. This is a direct decomposition via one reaction step: $H_2O(g) \rightarrow H_2(g) + {}_1/_2O_2(g)$. At equilibrium, the extent of this thermal decomposition depends primarily upon the temperature, but also upon the pressure of the steam-hydrogen-oxygen system. An inverse pressure dependence for the decomposition is evident from the fact that one mole of steam produces one and a half moles of gaseous products. The procedure of supplying high-temperature heat to steam to cause this decomposition has been suggested as a method for splitting water to produce hydrogen.[1,5]

The enthalpy required to convert water at 25°C and 1 atm to hydrogen and oxygen at 25°C and 1 atm, is 68.3 kcal/g-mol of hydrogen produced. In a process involving internal heat exchange, heat is needed to vaporize the water and to raise the temperature of the steam to the desired reaction temperature. Dissociation will occur continuously during this heating, and heat must be supplied for this reaction as well. Upon achieving satisfactory decomposition and having prevented recombination (by product separation), the latent heat of the product streams can be transferred to the cooler incoming reactant stream (water).

Temperature Dependence of Hydrogen Production

The temperature dependence of the dissociation may be related to the free-energy change of the dissociation reaction, ΔG_{Rx}, according to the conventional equation for the equilibrium constant, (for pressure) K_p:

$$\Delta G_{Rx} = -RT \ln K_p \qquad (8\text{-}3)$$

The equilibrium constant in Equation 8-3 is defined as —

$$K_p = \frac{(\text{Hydrogen Partial Pressure})(\text{Oxygen Partial Pressure})^{1/2}}{(\text{Water Partial Pressure})} \qquad (8\text{-}4)$$

The dissociation reaction may be expressed as —

$$H_2O(g) \rightarrow (1-x)H_2O(g) + xH_2(g) + 1/2xO_2(g)$$

where x is the number of moles of hydrogen present at equilibrium. Assuming that the partial pressures are equal to the mole fractions for the components simplifies the calculation determining the mole fraction of hydrogen present, y, as a function of temperature, provided the ΔG_{Rx} is known. Algebraically, $y = \frac{x}{1 + x/2}$. We have made this calculation to illustrate that relatively high temperatures are required for appreciable hydrogen production. The equation relating the equilibrium constant to the reaction stoichiometry is —

$$K_p = \left(\frac{x}{1-x}\right)\left(\frac{x}{2+x}\right)^{1/2} \qquad (8\text{-}5)$$

Table 8-1 is based on the tabulated enthalpy and free-energy data for water.[12] In Table 8-1, $\Delta H_{Rx}{}^T$ is the enthalpy required for the dissociation of one gram-mole of steam, and $\Delta G_{Rx}{}^T$ is the free energy of this dissociation. The hydrogen produced at equilibrium (at temperature T) is that amount resulting from the dissociation of one mole of steam at one atmosphere total pressure. (At lower absolute total pressures, the extent of dissociation is higher.)

Thermodynamic Considerations and Energy Requirements

The reaction enthalpy is often considered to be the ideal amount of energy, heat (entropy) plus work (free energy, G), that must be supplied to drive a chemical reaction. By analogy to electrolysis, entropy is usually supplied by resistive dissipation of electricty as heat, and free energy is supplied through ion and electron movement across an electrical potential, splitting water into hydrogen and oxygen. This is a case in which practical methods are approaching ideal limits.

In the case of thermal dissociation of steam, however, supplying the energy equivalent of the standard enthalpy, H, of formation (for water) does not accomplish the decomposition reaction or the required gas separations (to pure hydrogen and pure oxygen) at the reaction conditions. To illustrate this point, consider the dissociation of steam at 4310 ^{0}K, where ΔG_F^o of water is zero and ΔH_F^o is 61.06 kcal (heat)/g-mol. At this point, the equilibrium K_p is 1.0, and the product of the hydrogen partial pressure and the square

Table 8-1. THERMODYNAMIC DATA AND HYDROGEN YIELD FOR THE THERMAL DECOMPOSITION OF STEAM

Reaction Temp., T		Reaction Enthalpy, $\Delta G_{Rx}{}^{T}$	Reaction Free-Energy Change, $\Delta G_{Rx}{}^{T}$	Equilibrium Constant, K_p	Mole Fraction of Hydrogen Present, y (vol % ÷ 100)	Moles of Hydrogen Produced, x, Per Mole of Water Reactant
°K	°F	kcal/g-mol				
500	440	58.28	53.52	1.30×10^{-23}	7×10^{-16}	7×10^{-16}
1000	1340	59.25	46.04	8.67×10^{-11}	2.5×10^{-7}	2.5×10^{-7}
1500	2240	59.82	39.30	1.88×10^{-6}	1.92×10^{-4}	1.92×10^{-4}
2000	3140	60.15	32.40	2.88×10^{-4}	5.48×10^{-3}	5.50×10^{-3}
2500	4040	60.36	25.44	5.97×10^{-3}	3.76×10^{-2}	3.83×10^{-2}
3000	4940	60.53	18.44	4.54×10^{-2}	1.40×10^{-1}	1.51×10^{-1}
3500	5840	60.70	11.41	1.94×10^{-1}	2.90×10^{-1}	3.39×10^{-1}
4000	6740	60.91	4.35	5.78×10^{-1}	4.35×10^{-1}	5.56×10^{-1}
4500	7640	61.16	−2.73	1.36×10^{0}	5.30×10^{-1}	7.22×10^{-1}

root of the oxygen partial pressure equals the partial pressure of the undissociated water. Work (about 20 kcal/g-mol of hydrogen), must still be supplied to separate these components. If a hydrogen separation is not performed, rapid reaction kinetics will cause recombination (burning) as the gas mixture is cooled.

The free-energy change associated with separating gas mixtures at some temperature, T, or the ideal separatory work requirements may be calculated by Equation 8-6:

$$\Delta G_{sep} = -RT\Sigma X_i \ln y_i \qquad (8\text{-}6)$$

In this equation, X_i is the number of moles of component i present at mole fraction y_i. Calculations of ΔG_{sep} (required to produce one mole of pure hydrogen by thermal dissociation of water) show that ΔG_{sep}^{T} equals or exceeds ΔG_{Rx}^{T}. At 3500 ^{0}K, for example, ΔG_{sep} = 22.7 kcal/g-mol of hydrogen and ΔG_{Rx} = 11.4 kcal/g-mol of hydrogen.

Estimates of Theoretical and Ideal Energy Efficiencies

We have not considered, in detail, the thermodynamic efficiencies that have been or might be applied as limiting cases for the direct thermal decomposition of water. However, some discussion of this is in order because "ideal" efficiencies can appear particularly deceiving or overly optimistic when applied to direct thermal decomposition. The maximum theoretical, ideal water-splitting efficiency is [6,10]—

$$E_{ideal} = \frac{\Delta H}{\Delta G}\left(\frac{T_1 - T_2}{T_1}\right) \qquad (8\text{-}7)$$

where T_1 is the "high" temperature of heat supply and T_2 is the "low" temperature of heat rejection. This relation has been used in the context of thermal dissociation of water.[1] Its use here is not incorrect, but the relation is highly optimistic and requires restrictions. Obviously, if T_2 is held at 25 ^{0}C and T_1 is high enough, E_{ideal} will approach $\Delta H/\Delta G$ = 1.2. However, from the first law of thermodynamics it can be shown that negative heat rejection would occur to $T_1 > 1650\,^0$C and under all conditions of $E \leq 1.0$. (See Section 6.) Hence, it is advised that Equation 8-7, unaltered, not be used in setting an upper bound (ideal efficiency limit) for direct thermal water splitting.

To properly estimate the maximum attainable efficiency of direct thermal decomposition, and if heat is the primary energy source, all work-generating steps must be accounted for. One arbitrary way to postulate an energy efficiency limit for thermal decomposition (used by IGT in its hydrogen-production program) is to divide the high heating value (HHV) of the product hydrogen by the sum of the reaction entropy, the heat required to generate the reaction free-energy change, and the heat required to perform the extra separatory work (not satisfied by the supplied free energy). Separatory work is calculated for the composition and temperature of the decomposition. Table 8-2 presents these quantities based on an arbitrary 35% efficiency for work generation from heat (probably not appropriate for the 500 ^{0}K case). In our opinion, irreversibilities and heat losses would result in practical efficiencies of about 50% to 65% of those listed for T >2000^0 K, assuming that process equipment and plant materials could be used with performance similar to that attained with modern technology. For T < 2000 ^{0}K, the separatory equipment for recovering the very small concentrations of hydrogen produced would be excessive in complexity and in energy consumption. Thus, practical efficiencies would be very low for temperatures below 2000 ^{0}K.

In 1972, The Futures Group prepared a hydrogen technology assessment for the Northeast Utilities Service Co. [5] In that report, they summarized their analysis of a water dissociation system operating at 5000 ^{0}F (3033 ^{0}K) and at 1 atm. Steam was forced through a vortex tube at high velocity, and the hydrogen was separated from the steam and oxygen. The hydrogen stream and the water plus oxygen stream were cooled to condense the steam and separate the gases; the condensation was taken through 10 stages for 90% heat recovery. The efficiency of this system, based on heat and mass balance, "was computed to be only 35%."

The recent study by Bilgen[1] considers solar energy as a heat source for direct thermal dissociation of water. However, no particular process or flow diagram was analyzed. The author does conclude that 3000 ^{0}K heat is required "for a substantial yield in hydrogen production." A general description of solar concentrators, with cost estimates, is presented for components capable of high temperatures. Bilgen is optimistic about being able to achieve suitably high temperatures with a combination of a mirror field and concentrating units and states that 3500 ^{0}K should be achievable.

Table 8-2. ESTIMATED UPPER EFFICIENCY LIMITS FOR DIRECT THERMAL DECOMPOSITION OF WATER

Reaction Temp., T		Reaction Entropy	Heat for Free Energy	Heat for "Extra" Work	Efficiency Limit Based on HHV of Hydrogen, %
°K	°F	kcal/g-mol			
500	440	5.92	152.9	0.0	43
1000	1340	13.21	131.5	0.5	47
1500	2240	20.54	112.3	3.5	50
2000	3140	28.11	92.6	11.1	52
2500	4040	34.92	72.7	17.4	55
3000	4940	42.09	52.7	24.6	57
3500	5840	49.29	32.6	32.3	59
4000	6740	56.56	12.4	43.7	61
4500	7640	58.43	0.0	49.1	63

References Cited in This Section

1. Bilgen, E., "On the Feasibility of Direct Dissociation of Water Using Solar Energy," EP 75-R-10. Montreal: Ecole Polytechnique de Montreal, January 1975.

2. Bylinsky, G., "KMS Industries Bets Its Life on Laser Fusion," Fortune 90, 149-56 (1974) December.

3. Eastlund, B. J. and Gough, W. C., "The Fusion Torch," Wash-1132. Washington, D.C.: U.S. Atomic Energy Commission, May 1969.

4. Eastlund, B. J. and Gough, W. C., "Generation of Hydrogen by Ultraviolet Light Produced by the Fusion Torch." Paper presented at the 163rd Meeting of the American Chemical Society, Boston, April 9-14, 1972.

5. Fein, E., "A Hydrogen-Based Energy Concept," Rep. No. 69-08-10, prepared for Northeast Utilities Service Co., p. 33. Glastonberry, Conn.: The Futures Group, October 1972.

6. Funk, J. E., Reinstorm, R. M., "Energy Requirement in the Production of Hydrogen from Water," Ind. Eng. Chem. Process Design and Development, 5, 336-342 (1966) July.

7. Gomberg, H. J., Comments at the World Energy Conference, Detroit, September 1974.

8. Harteck, P. and Dondes, S., "Producing Chemicals With Reactor Radiations," Nucleonics 14, 22-25 (1956) July.

9. Juppe, G., "Chemonuclear Reactors," Eur. Spectra 8, 39-45 (1969).

10. Pangborn, J. and Sharer, J., "Analysis of Thermochemical Water-Splitting Cycles," Paper presented at THEME Conference, Miami, March 1974.

11. Stein, G., The Chemistry of Ionization and Excitation, pp. 27, 28. University of Newcastle Upon Tyne: Johnson and Scholes, September 1966.

12. Stull, D. R. and Prophet, H., Eds., JANAF Thermochemical Tables, Second Edition. Washington, D.C., 1971.

13. Ung, A. Y. M. and Back, R. A., "Photolysis of Water Vapor and Reactions of Hydroxyl Radicals," Can. J. Chem. 42, 753-63 (1964).

14. Von Fredersdorff, C. G., "Nonfossil Fuel Process for Production of Hydrogen and Oxygen," U.S. Ser. 211,960 (1971) December 27.

9. COMMERCIAL TECHNOLOGY FOR HYDROGEN PRODUCTION — T. D. Donakowski

Catalytic Steam Reforming of Natural Gas

Steam reforming of natural gas is the most widely used hydrogen manufacturing process in the United States.[3] Commercial operations began in 1930 after a 15-year development period. A typical process for a large, modern hydrogen-production facility is discussed below and is illustrated in Figure 9-1.

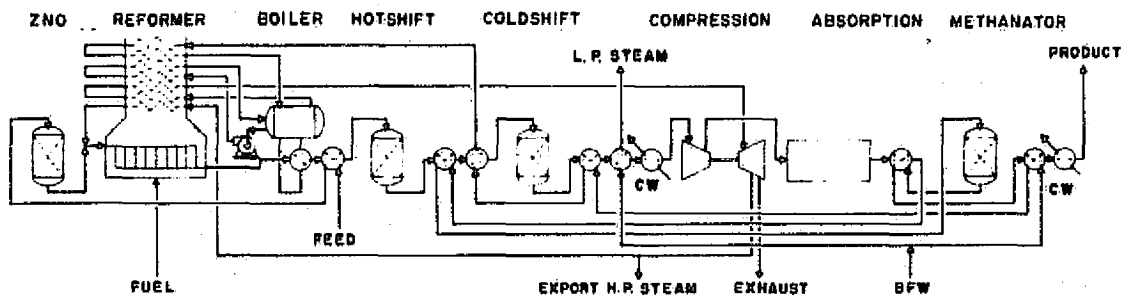

Figure 9-1. FLOW DIAGRAM OF A STEAM-REFORMING PROCESS[1]

The primary step in the production of hydrogen from natural gas is the endothermic steam-methane reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

To reduce any catalyst-poisoning sulfur compounds to a level of less than 5 ppm,[1] the natural gas is passed through a sulfur guard drum that contains zinc oxide. The sulfur-free natural gas is combined with superheated steam, thus forming the feed for the reforming furnace. (Steam-to-methane ratios are usually 3:1 or 4:1, by volume.) The steam is then passed through a vertical array of type 25-20 chrome-nickel steel tubes that contain a catalyst. A typical commercial catalyst is composed of nickel oxide on a refractory substrate. The catalyst may be shaped into pellets 1/2 to 3/4 inch in diameter and length or into Raschig rings of similar size.

Reforming has been performed at pressures up to 600 psi, but 300 psi is typical. If a high-pressure hydrogen product is desired, it is preferable to reform the natural gas at a high pressure. The reforming reaction increases the volume of the gas, so less compression is required if the feed is initially at high pressure. However, high pressures require high

temperatures to ensure a favorable equilibrium. A more efficient recovery of heat from the product gas is attained at the higher temperatures. Gas typically exits the reforming furnace at temperatures of from 1500° to 1650°F. The equilibrium constant for the steam-methane reforming reaction increases by a factor of 3 as the temperature is increased from 1470° to 1560°F, so temperature is an important process operating parameter.[3] Heat is transferred to the reformer furnace tubes from the radiant section of the furnace, and large amounts of heat are available for steam generation in the convection section.

The reformed gas is composed of hydrogen, water, carbon monoxide, carbon dioxide, and residual methane. It is cooled to about 700°F and is passed through a shift reactor in which excess steam reacts with carbon monoxide to form carbon dioxide and more hydrogen via the exothermic reaction —

$$CO + H_2O \rightarrow CO_2 + H_2$$

An iron oxide-chromium oxide catalyst is used. The equilibrium constant for this reaction increases with a decrease in temperature, and at 700°F, a satisfactory conversion of carbon monoxide to hydrogen cannot be achieved. A second shift reactor is used that operates at temperatures of from 350° to 450°F and that utilizes a low-temperature catalyst containing copper, chromium, and zinc oxides. This low-temperature catalyst is permanently damaged if it is used at temperatures higher than design.[3]

The shifted gas stream is then compressed, typically with steam-turbine-driven centrifugal compressors, and enters a carbon-dioxide-removal system. In choosing a carbon-dioxide-removal system for the process, the desired purity of the product and the inlet pressure of the absorber feed-gas must be considered. Several absorption processes are commercially available (e.g., monoethanolamine and hot-potassium-carbonate systems).

Finally, if desired, traces of carbon oxides can be removed by reacting the gas with hydrogen to form methane via the exothermic reactions —

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

and

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The reactions occur in the presence of a nickel catalyst at from 750° to 840°F and at pressures of up to 600 atmospheres. Water is removed, thus leaving

the hydrogen product (typically 97% pure).[1] A process and utility summary for the steam reforming of natural gas is presented in Table 9-1.

Table 9-1. EFFICIENCY, PROCESS, AND UTILITY REQUIREMENTS OF STEAM REFORMING NATURAL GAS FOR THE PRODUCTION OF 97% - PURE HYDROGEN
(Per 1000 SCF of Hydrogen)[3]

		Amount
Process Feed, lb of methane		11.9
Fuel, lb of methane		7.9
Electric Power, kWhr		0.4
Cooling Water, gal		400
Boiler Feedwater, gal		10
Condensate Returned, gal		6
Input 19.8 lb of methane X 23,880 Btu/lb	=	472,800 Btu
0.4 kWhr Electricity X 3414 Btu/kWhr	=	1,400 Btu
Total		474,200 Btu
Output = 1000 SCF of Hydrogen X 325 Btu/SCF	=	325,000 Btu

$$\text{Efficiency} = \frac{\text{Output}}{\text{Input}} = \frac{325,000}{474,200} \times 100$$

$$= 68.5\%$$

Partial Oxidation of Hydrocarbons

There are two partial-oxidation processes that have been extensively commercialized: the Texaco Process (since 1954) and the Shell Gasification Process (since 1956). Gas consisting primarily of hydrogen and carbon monoxide is produced by burning hydrocarbons with high-purity oxygen or an oxygen-rich stream. The main processing features of the Texaco Process are shown in Figure 9-2 and are discussed below.

High-purity oxygen (95% to 99%) is injected into the gas generator, along with preheated steam and heavy oil (10^0 API gravity). Proper metering of the feed into the specially designed mixing burners is essential. A typical steam-to-oil weight ratio would be 0.5:1. It should be noted that oxygen and oil are not premixed; therefore flashbacks and limits to preheat are not encountered. A high degree of steam and oil preheat is desirable because it significantly reduces the oxygen requirement.[3] The use of less oxygen results in the presence of less diluent nitrogen in the final hydrogen product stream.[2] Any percentage of sulfur in the oil feed is permissable, although the efficiency

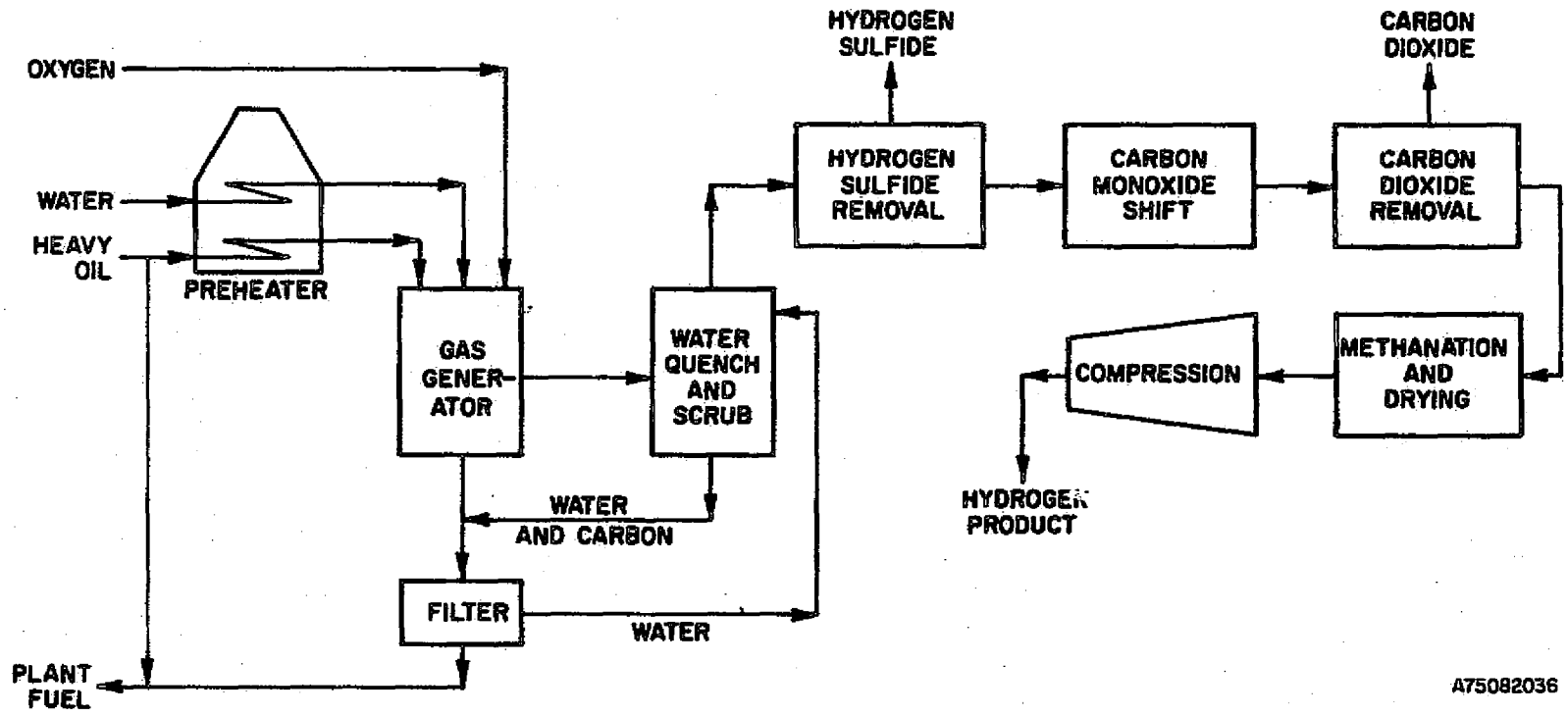

Figure 9-2. TEXACO PARTIAL-OXIDATION PROCESS
(Heavy Oil to Hydrogen)[2]

of hydrogen production is lower for a higher sulfur-content oil than for a sulfur-free oil because hydrogen is consumed in the removal of sulfur as hydrogen sulfide. A refractory-lined reactor is used to withstand the 2500°F final gas-generation temperature. The Texaco gas-generating reactor can be run at pressures of between 200 and 600 psi. Better compression economics can be obtained if the gasifier is operated at high pressure because the gaseous volume of the feed materials is less than the volume of the hydrogen generated. Heat from the reactor is used for internal generation of steam via a water-quenching step. The steam is subsequently reacted in a carbon monoxide-water shift step. The water quench also removes particles of unreacted carbon, which are recovered by filtration and can be mixed with oil for plant fuel requirements.[3]

The synthesis gas then undergoes aftertreatment steps, similar to the steps undergone downstream in a steam-natural gas reforming process, to increase the amount and the purity of the hydrogen. Hydrogen sulfide is removed; and the stream is shifted, in a carbon monoxide conversion step, to produce more hydrogen. Carbon dioxide is removed from the hydrogen by an absorption process. If desired, final traces of the carbon oxides can be removed by reaction to methane; and finally water is removed from the system. The hydrogen can then be compressed to the required pressure.

References Cited in This Section

1. Beavon, D. K. and Roszowski, T. R. "Modern Hydrogen Manufacture." Paper presented at the Division of Petroleum Chemistry Symposium on Hydrogen Manufacture – Chemistry and Catalytic Technology, American Chemical Society, Los Angeles, March 28-April 2, 1971.

2. Janka, J., Arora, J., Tsaros, C., Fore, J., Kester, F. and Gregory, D., "An Evaluation of the Present Technology for Production of Pure Hydrogen From Coal," Final Rep. for MAPCO, Inc. Chicago: Institute of Gas Technology, March 1974.

3. Standen, A., Ed., Kirk-Othmer Encyclopedia of Chemical Technology Second Ed., Vol. II, pp 347. New York: Interscience Publishing 1966.

10. SURVEY OF PATENTED HYDROGEN-PRODUCTION PROCESSES – H. C. Maru

In order to complete this survey of hydrogen-production processes, we examined the literature with the hope of finding novel processes that had been suggested, but that had never been fully developed. We anticipated that, in the past, the ease of making hydrogen by steam reforming relatively cheap natural gas would have made the development of other hydrogen processes unattractive; but that now, with the supply of natural gas rapidly dwindling, these processes might be worthy of attention.

Ideally, search of this type would involve a complete literature review and evaluation. However, the number of literature entries on hydrogen production is immense, and a comprehensive search of all published literature was out of the question. We decided to proceed on the assumption that if a novel hydrogen-production method had not been developed, it would at least have been patented.

We conducted a search through abstracts of patents published in Chemical Abstracts from 1917 to 1974 using the following key words appearing under the heading, "Hydrogen":

- Formation of
- Manufacture of
- Preparation of
- Production of.

We limited our attention to those processes that made either pure hydrogen or significant amounts of hydrogen mixed with nitrogen, carbon monoxide, and/or carbon dioxide because these mixtures could easily be converted to pure hydrogen.

Literature prior to 1917 was scanned through two important monographs dealing with hydrogen production.[5,14] Increased activity of the recent years has been documented in several symposia proceedings[1,17,18] and compilations.[4,7] These documents were also scanned for this survey.

Classification of Processes

The number of relevant patents found was staggering. We had expected that only about 200 or so processes would have been patented in the last 60 years. Instead, we found about 1800 patents.

We sorted the patents into 10 categories, as shown in Table 10-1. Patents relating to purification schemes, storage, safety, or corrosion and those describing hardware or control equipment were rejected. Approximately 56% of the total number of patents related to hydrogen production from hydrocarbons, 22% related to coal, and 7% related to water electrolysis. The patents related to unconventional hydrogen-production processes were assigned to a general category, "Other Sources."

Table 10-1. CLASSIFICATION OF PATENTS FOR HYDROGEN PRODUCTION

Category	Code	Number of Patents	% of Total
Electrolysis of Water	E	128	7
Electrolysis of Impure Water and Other Solutions	I	47	3
Coal and Related Sources	C	394	22
Hydrocarbons and Fossil Fuels	H	985	56
Oil Shale	K	9	0.5
Synthetic Fuels	F	29	2
Thermochemical	T	10	0.5
Solar, Windpower, Geothermal, and Ocean Thermal Gradients	S	2	--
Waste Materials	W	9	0.5
Other Sources	O	157	9
Total		1770	
Patents Rejected (Not Processes)		500	
Total Examined		2270	

The patents in each category were arranged alphabetically by assignee organization (or by author if the patent was not assigned to an organization). The purpose of this arrangement was to assemble all the patents related to a single process, thus allowing us to judge the state of development of each process and to eliminate duplication. The patents, so arranged, are listed in Appendix C.*

Evaluation of Processes

After classification and arrangement, the patents in each category were evaluated by an IGT expert in the particular field in order to find any promising processes. All the patents and literature were further reviewed by the chemical engineer in charge of the patent survey. Figure 10-1 is a schematic flow diagram of the procedure used for this survey.

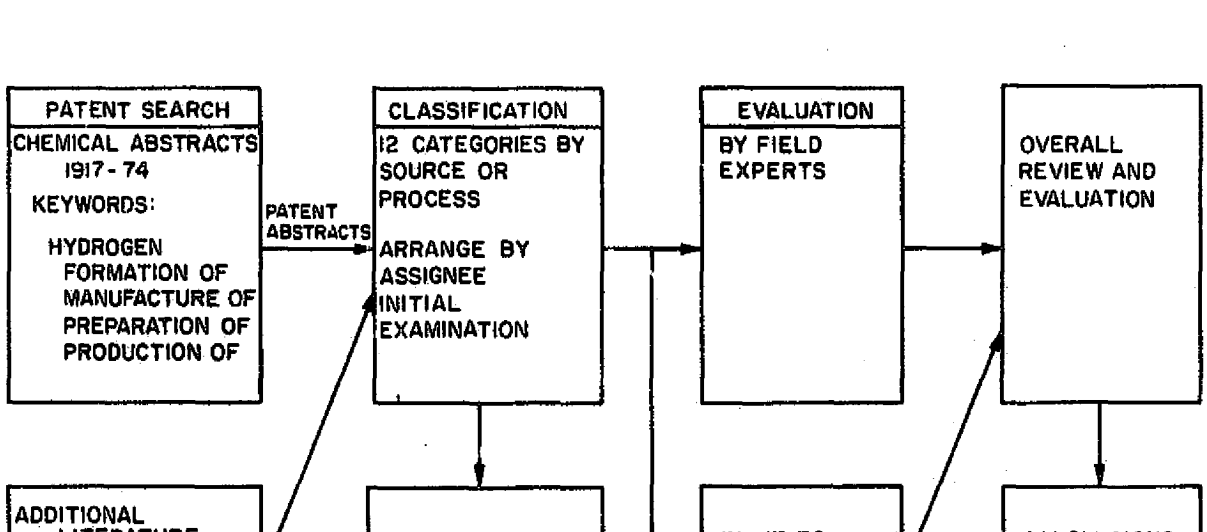

Figure 10-1. FLOW DIAGRAM OF LITERATURE SURVEY OF HYDROGEN-PRODUCTION TECHNIQUES

*An alphanumeric code has been assigned to each patent, as explained in Appendix C. References to these patents in the text are made using this nomenclature.

Several novel processes and suggestions were identified as being worthy of further consideration. Because of the large number of patents retrieved (approximately 10 times the number originally anticipated), by mutual agreement with NASA only the novel processes and suggestions have been cataloged in detail. Many of the processes currently under development are discussed in other sections of this report.

Electrolysis of Pure Water

Several patents describe means of increasing the current density and efficiency of electrolysis via minimization of electrode overvoltages and ohmic polarizations. Recently, processes that use thermally aided electrolysis have been proposed.[3]

Overvoltage Reduction

Several proposed methods of electrode and electrolyte modification are described in Table 10-2. As can be seen in this table, improvements of as much as several hundred millivolts have been claimed.

A patent by DEMAG Electrometallurgic GmbH (ED3) sugggests additions of wetting agents to facilitate bubble removal, thereby minimizing concentration polarization. A patent by E. G. Clark (EC4) claims that current densities as high as 7200 A/sq ft can be achieved when the electrolyte is forced through a thin layer placed between the electrodes. A somewhat different flow-through electrode system is being tested at Brookhaven National Laboratories.[10] Large drops in pressure and structural difficulties in manifolding are anticipated with this concept. At present no commercially operating system uses such a concept.

Because oxygen polarization is a major factor in many water electrolyzer cells, several depolarization schemes have been suggested.[3,8] The patents by General Electric Co. (EG3) and H. H. Moebius and B. Rohland (EM10) suggest putting a reducing gas (e.g., producer gas) in a solid-oxide system to depolarize the oxygen electrode. Juda and Moulton[8] suggest adding sulfur dioxide in the form of sulfurous acid in an acid-electrolyte cell. A voltage gain of about 800 mV has been claimed for such a system. Additional corrosion and contamination problems and the added cost of a depolarizing agent are the trade-off considerations. Recently Bockris[2] suggested the use of this concept for simultaneous pollution cleanup, where, for example, nitric

Table 10-2. PROPOSED ELECTRODE AND ELECTROLYTE MODIFICATIONS

Assignee or Author	Reference*	Electrolyte	Electrode† Hydrogen	Electrode† Oxygen	Proposed Method	Claimed Improvements
Clark, E.G.	EC4	NaOH	X	X	Forced electrolyte flow through spaces between the electrodes	Obtain a C.D. of 7200 A/sq ft
Consolidated Mining and Smelting of Canada Ltd.	EC6	Caustic alkali	--	--	Vanadium in sol. form (e.g., V_2O_5) added to electrolyte	Cell voltage reduced
DEMAG Elecktro-metallurgie, GmbH	ED3	Aqueous solutions	X	X	Wetting agents to facilitate bubble removal, silicone oils added to fatty acid to prevent foaming	Lower concentration polarization
East Asia Synthetic Chemical Industries Co.	EE2	18% NaOH	--	--	0.05 g/l $(NH_4)_2SO_4$ added to electrolyte, other S compounds – e.g., $(NH_4)CNS$ or $(NH_2)_2CS$ – can be used.	Lowered total cell volume by 20 mV at 50 mol/sq cm
General Electric Co.	EG3	Solid oxide		X	Reducing gas mixture to depolarize oxygen electrode	Lower oxygen overvoltage
Imperial Chemical Industries of Australia and New Zealand Ltd.	EI3		X		(Mo, W)-(Fe), (Mo)-(Ni, Co) or (Mo)-(Co, Ni, Fe)-(Co, Ni, Fe), and (Ti-Pt) coatings electrodeposited	A W-Fe coated electrode resulted in 80 mV decrease in overpotential; an Mo-Co rated electrode resulted in 150 mV decrease in overpotential
Juda, W. and Moulton, D.M.	Ref. 8	Aqueous acidic		X	Add SO_2 in the form of H_2SO_3	800 mV lowering of polarization
Lonza Elektrizitäts-werke	EL13		X		Electroplating Pt, Rh, Pd, Os, or Ir on Fe cathode; reactivation by OCV operation	Several hundred mV lowering in H oversalt
Maschinenfabrik Oerlikon	EM3		--	--	Compound of sixth group metal of Na_2MoO_4	Overvoltage reduction
Moebius, H.H. and Rohland, B.	EM10	Solid oxide		X	Reducing gas mixture to depolarize oxygen electrode	Lower oxygen overvoltage
Pintsch Bamag AG	EB1	KOH (?)	--	--	Deposit alloy (e.g., Zn-Ni-Cu) from a bath containing a complex-forming reagent such as a cyanide, pyrophosphate on sulfamate: activate by partly dissolving a first component of the alloy (e.g., Zn) in an alkali or cyanide solution.	Surfaces not pyrophoric, greater flexibility in selection of structural and final shape
Siemens and Halske AG	ES17		X		Cathode treated with an electrolyte containing metallic oxygen acids – e.g., chromates, molybdates, tungstates, columbates, titanates; alternatively, add small amounts to cathode chamber.	The compounds dissolve, but do not decompose; lower overvoltage
State Pedagogical Inst., Kharkov, U.S.S.R.	ES21		X		Alloys of Ni-Ru or Co-Ru applied on a metal base consisting of Fe, Ni, Cu, or Ti	Lower hydrogen overvoltage
Tseung, A.C.C. and Vassie, P.R.	Ref. 16	KOH		X	Co_2NiO_4 catalyst	High anode activity, stable performance at room temperature
Werlen, A. et al.	EW1		X	X	Hg-Cu-Zn catalyst on anode and an alkali phosphate as depolarizer on Al cathode	

*Unless otherwise noted, refers to Appendix C.

†Where known, the electrode(s) considered for modification is denoted with an "X."

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oxide can be oxidized to nitric acid or sewage can be oxidized to carbon dioxide. The resulting cost reductions in the depolarized-anode systems may be attractive.

Alternatively, to minimize the oxygen overvoltage, Tseung and coworkers[15,16] have reported the use of a highly active electrode catalyst. A rapid electrode deactivation was observed when operated in the fuel cell mode,[15] but stable performance for several hundred hours was obtained at room temperature when operated in the oxygen-evolution mode.[15]

Electrolyte Systems

Electrical conductivity and electrode kinetics can be improved by the use of suitable electrolytes. An Atlantic Richfield Co. patent (EA6) claims operation of a molten-alkali electrolyte cell at 1.3 volts (an apparent efficiency of 113%) and at current densities of 500 mA/sq cm with use of a 90% calcium hydroxide, 10% sodium hydroxide electrolyte at 480°C. Problems of corrosion, electrode sintering, and performance stability are anticipated. Another patent (EB5) claims use of molten sodium hydroxide or potassium hydroxide containing 5% to 10% water. The cell in this case was operated at 300° to 350°C and iron electrodes were used.

The use of solid-oxide electrolytes at high temperatures has also been proposed[13,19] (EG3 and EM10) for water-vapor dissociation. Higher efficiencies and rapid electrode kinetics can be obtained at high temperatures; but research shows some major problems: thermal stresses in the ceramic electrolytes, retention of sufficient electrolyte purity to avoid the onset of semiconducting properties, selection of metals for the electrode at the oxygen side in the 800° to 1000°C operating range, and difficulty in finding materials suitable for intercell current collectors. Because of these problems, almost all research on this type of system has been abandoned. Bockris[3] suggests that even if these problems were solved, the cost of high-temperature electrolyzers would be about the same as that of low-temperature electrolyzers currently being developed. Therefore, research on moderate-temperature (80° to 400°C) electrolyzers should be emphasized.

Cell Design

Two patents (EA5 and EU2) claim a cell design suitable for zero-gravity operation. One patent issued to Reynolds Metals Co. (ER1) is for a cell

designed to produce gases under hydrostatic pressure with the gases collected outside the vessel. Several high-pressure units that use pressure vessels for pressure containment have been built, for special applications, by Construction John Brown Ltd. of Great Britain.[11, 12] Such designs, however, may not be cost effective for large-scale production because of the high containment-material cost compared with that for diaphragm-type cells.

System Design

A Swedish patent (ES24) claims a modification that purifies a contaminated electrolyte by electrolyzing the impure electrolyte in a mercury cell and subsequently decomposing the amalgam with water to obtain an alkali solution. The modification would, however, involve additional investment for a mercury cell. Therefore adopting such a modification is a question of relative economics.

A vapor-diffusion water feed arrangement has been suggested in a patent by TRW, Inc. (ET1). An in situ purification system that uses a palladium coating on the electrode is suggested in patent ET3. A patent by A. Kilgus (EK3) claims hydrogen yields, upon application of a magnetic field to the electrolyzer, in excess of those determined by Faraday's Law. The validity of this claim is doubtful; but even if this were true, the additional energy used and the complications in maintaining a magnetic field would compensate for the additional yields.

Thermally Assisted Electrolysis

The electrolysis of water at a pressure of 1 atmosphere and at 25°C requires a minimum potential of 1.23 volts. Because electricity cost is a major component in the overall hydrogen cost, electrolysis of an alternative substance that has a lower reversible cell potential than water and subsequent thermal decomposition of the products is tempting. Greater overall efficiencies may be possible in such cases. Bockris[2] has suggested four such systems:

1. Electrolysis of hydriodic acid (HI) –

   a) Electrochemical step $2HI \rightarrow H_2 + I_2$ $\Delta E_{25}^{o} = 0.535$ volt

   b) Thermal step (endothermic) $I_2 + H_2O\ (1400^{o}C) \rightarrow 2HI + 1/2O_2$

2. Electrolysis of cuprous chloride (CuCl) in a cell containing hydrochloric acid (HCl) —

a) Electrochemical step
$2Cu^{+} \rightarrow 2Cu^{2+} + 2e^{-}$
$2H^{+} + 2e^{-} \rightarrow H_2$ $\quad \Delta E_{25}^{o} = 0.535$ volt

b) Thermal steps (endothermic)
$2CuCl_2 \rightarrow 2CuCl + Cl_2$ $\quad \Delta E_{25}^{o} = 0.77$ volt
$Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

3. Electrolysis of ferrous chloride ($FeCl_3$) in a cell containing HCl—

a) Electrochemical step
$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^{-}$
$2H^{+} + 2e^{-} \rightarrow H_2$ $\quad \Delta E_{25}^{o} = 0.535$ volt

b) Thermal steps (endothermic)
$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$
$Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

4. Electrolysis of stannous chloride ($SnCl_2$) in a cell containing HCl —

a) Electrochemical step
$Sn^{2+} \rightarrow Sn^{4+} + 2e^{-}$
$2H^{+} + 2e^{-} \rightarrow H_2$ $\quad \Delta E_{25}^{o} = 0.77$ volt

b) Thermal steps (endothermic)
$SnCl_4 \rightarrow SnCl_2 + Cl_2$
$Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

Several practical limitations exist, but because there is the potential of minimizing the electrical energy use, thermally assisted electrolysis systems deserve a closer look. According to Bockris's estimate, systems 1, 2, and 4 may be more economical than the advanced water electrolyzer systems. It is noted here that the high-temperature, direct water electrolysis processes may also consume heat and in that sense can be considered thermally aided electrolysis processes.

Electrolysis of Impure Water and Other Solutions

Our literature search produced four patents (IM3, IO1, IS6, and IT6) related to the direct electrolysis of seawater. The patents claim various means for minimizing the problem of insoluble deposits. Seawater electrolysis has been used for the in situ generation of hypochlorites for use as sterilants. Countries such as Japan use concentrated seawater brine for chlor-alkali production.[9] Thus some experience has been gained in seawater electrolysis. A more detailed discussion of the problems in direct seawater electrolysis is presented in Section 3.

When electrolyzed, aqueous solutions of many salts (such as sodium chloride), sulfates, or acids (such as hydrochloric acid) yield hydrogen as a byproduct. Because this technology is well developed, some of the advances made in this field, such as membranes and electrode technology, may be beneficial to pure- and impure-water electrolyzer systems.

Among the patents retrieved in the present survey is a patent by Matushita Electric Industries Co. (IM1) that suggests the electrolysis of an aqueous solution of ammonium chloride (NH_4Cl) or ammonium nitrate (NH_4NO_3) in the presence of semiconductor powders for the production of high-purity hydrogen. A patent issued to Asahi Chemical Industry (IA3) proposes the addition of platinum or palladium to the electrolyte. An 0.8-volt polarization decrease resulted.

Coal and Related Sources

Most of the 300 or so patents in this category deal with established coal-gasification processes that produce, as a first step, a mixture of carbon monoxide and hydrogen. Fluidized-bed gasification, such as that used in the Winkler and HYGAS® Processes, is often mentioned. Many of the other patents describe suspension gasification processes similar to those being developed by Texaco and those offered for sale by Koppers-Totzek. Some of the patents are for modifications to the steam-iron process — an improved form of which, described in an earlier section, is currently under development for use in coal gasification. These patents often suggest the use of another metal as the oxidizing-reducing agent.

The production of clean gaseous fuels from coal has been intensely researched in the past few years. Consequently it should not be surprising that all of the promising ideas described in this group of patents are currently under development.

Hydrocarbons

This category, largest among the categories surveyed, includes approximately 1000 patents on hydrogen production from fossil hydrocarbons such as natural gas, naphtha, or other petroleum components. The majority of the patents in this category were issued after 1940. The processes include catalytic steam reforming, catalytic and noncatalytic partial oxidation, and

thermal decomposition. Because of the rapidly depleting world supply of petroleum and natural gas, their role in future hydrogen production will be limited. The large number of patents in this field is indicative of the amount of research and development that has been carried out, and it is unlikely that any promising processes have been neglected. For these reasons, these patents were merely summarized and listed without further examination. Patents on hydrogen production from oil shale were classified separately, however, because of the possibly significant role of this source as a future energy supply. Patents applicable to multiple sources, such as hydrocarbons, coal, carbon monoxide, and coke, were included in the category "Coal and Related Sources."

Organizations holding large numbers of patents on the production of hydrogen or hydrogen-rich gas from hydrocarbons include I. G. Farbenidustrie (on thermal decomposition of gaseous hydrocarbons), Standard Oil Co. (on the reforming of light hydrocarbons and thermal decomposition of a variety of hydrocarbon liquids), Texaco, Inc. (on partial oxidation), and Badische Anilin and Soda Fabrick (on partial oxidation). These patents describe variations in process conditions (temperature, pressure, etc.), catalysts, reactor designs, and process steps.

Some exotic suggestions, such as the electrolysis of hydrocarbons and the simultaneous production of mechanical energy, were also encountered. Many of the more recent patents describe hydrogen production on a small scale for local application such as self-propelled vehicles, fuel-cell operation in residences or small industries, for special appliances or equipment, and for laboratory or experimentation purposes.

Oil Shale

Our literature search, using the keywords mentioned previously, yielded only nine patents that deal with hydrogen production from oil shale. The patent issued to Chevron Research Co. (KC1) describes a process that uses steam injection for hydrogen production from kerogen-depleted shale formations. The patent issued to Compagnie Francaise des Essences Synthetiques (DC2) claims the coke-free production of hydrogen-rich gas from oil shale and other solid fuels. The Institute of Gas Technology patents (K11, K26, K23, and K24) deal with hydrogasification steps and reactor designs. Hydrogen is obtained as a coproduct in the process patented by P. H. Gifford (KG1). Two patents

issued to Phillips Petroleum Co. (KP1 and KP2) describe their partial-combustion process and the utilization of carbon monoxide from the combustion zone for the production of hydrogen.

Synthetic Fuels

This category includes the production of hydrogen from synthetic organic compounds such as methanol, acetylene, ethanol, cyclohexane, and heptane. Because these compounds are usually synthesized by using petroleum, coal, or other fossil fuels, they will probably not be used for large-scale hydrogen production. Methanol, however, has been recognized as a convenient portable fuel. Because of the low reforming temperatures involved, simple materials of construction, and good catalyst stability, it can be reformed at the point of application to produce hydrogen. Fuel cells and automotive fuel are two examples of such applications. Hydrogen is obtained as a byproduct in the thermal dissociation of acetylene to produce carbon black. Of the patents retrieved, a majority of the patents covered these two sources.

Two patents issued to the U.S. Atomic Energy Commission (FU3, and FU4) claim the cracking of hydrocarbons by using x-rays or neutron bombardment. A patent issued to Varta A.G. (FV1) claims the simultaneous production of oxygen and hydrogen by utilizing heat released by the oxygen-generating compound to catalytically decompose the hydrogen-generating compound. Such an arrangement can be beneficial in generating gases for fuel cell or welding equipment.

Thermochemical Hydrogen Production

Our patent search retrieved only 10 patents for this category. It is likely that many cycles have not been patented, and others may be in the process of being patented. The patents retrieved include EURATOM's mercury-hydrobromic acid (Hg-HBr) cycle, Gaz de France's stannous oxide-stannic oxide (SnO-SnO_2) cycle, and others.

In addition to the purely thermochemical cycles, several hybrid cycles have been suggested. The thermally aided electrochemical processes discussed previously are examples of such hybrid cycles.

Solar, Windpower, Geothermal, and Ocean Thermal Gradients

Only a small fraction of the energy available from solar, wind, and geothermal sources is currently being utilized for energy conversion. Several possibilities for utilizing these important sources exist.

Solar radiation can decompose water through either thermochemical, photochemical, photoelectrochemical, or photobiochemical routes.

Direct generation of hydrogen by the use of wind power is not possible. Windpower is first converted to electricity, which then can be used for electrolysis. Geothermal energy could also be converted to electricity for electrolysis, but there is the additional possibility of matching a low-temperature thermochemical cycle to the heat source.

Because the interest in possible applications of solar, windpower, and geothermal sources to hydrogen production is of recent origin, no patent literature exists in this field. Only two patents that deal with system concepts were retrieved. Patent SK1 proposes high-pressure electrolysis as a means of energy storage for solar, wind, or tide energy. (Hydrogen is subsequently converted to ammonia, which is stored.) Patent SO1 claims utilization of windpower in the electrolysis of seawater for hydrogen production. Escher[6] recently proposed an ocean-based, solar-to-hydrogen energy conversion macrosystem. Researchers in several government-sponsored programs are currently exploring the use of these abundant natural sources in hydrogen generation.

Waste Materials

Nine patents were found that were primarily concerned with the production of hydrogen or hydrogen-rich gases from waste materials. Six of these patents (WC1, WC2, WF1, WR1, WS1, and WT1) deal with some form of gasification. The other three deal with fermentation (bioconversion). A considerable amount of patent and other literature exists on gas-production processes. These processes can be suitably modified to produce hydrogen. However, no special literature search was conducted to explore this aspect.

Other Sources

Patents not falling into any of the categories discussed previously were classified as "Other Sources." Patents in this classification were further subdivided by types of reactions, as shown in Table 10-3. Generally, the

Table 10-3. HYDROGEN-PRODUCTION TECHNIQUES USING "OTHER SOURCES"

Subdivision	Description	Number of Patents	Typical Reactions
1	Hydrides and boranes	23	$LiH + H_2O \rightarrow H_2 + LiOH$
			$BH_3(NH_2)_2\ BH_3 + LiBH_4 \rightarrow H_2$ + borohydrides
2	Caustics (silicon and iron	19	$2NaOH + Si + H_2O \rightarrow 2H_2 + Na_2SiO_3$
3	Metals	15	$H_2O + Al + KOH \rightarrow 3/2\,H_2 + KAlO_2$
4	Nonmetals	41	$2H_2O + S \rightarrow 2H_2 + SO_2$
5	Ammonia	28	$2NH_3 \rightarrow N_2 + 3H_2$
			$NH_3 + O_2 \rightarrow 3/2\,H_2$ + nitrogen oxides
6	Inorganic compounds	6	$H_2O + CaC_2 \rightarrow H_2 + 2C + CaO$
7	Miscellaneous	25	$H_2S + 2CO_2 \rightarrow H_2 + 2CO + SO_2$
			$S + 2H_2O \xrightarrow{e^-} 2H_2 + SO_2$
			$H_2S + O_2 \rightarrow H_2 + SO_2$
	Total	157	

patents in this classification describe methods of hydrogen production for special applications, such as onsite welding-gas generation, balloon inflation, torpedo-propulsion systems, and fireworks displays. The processes are energy-inefficient in hydrogen production, either requiring complex starting materials and catalysts or producing hydrogen only as a byproduct. For the most part, they are convenient for the intended use, but are neither practical nor economical for large-scale production. However, some methods may be beneficial in the development of hydrogen-storage concepts (e.g., metal-hydride containment) and might have possible uses within closed-loop thermochemical reactions. No unconventional processes for large-scale hydrogen production were uncovered in this category.

References Cited in This Section

1. American Society of Mechanical Engineers, Ninth Intersoc. Energy Convers. Eng. Conf. Proc., San Francisco, August 1974.

2. Bockris, J. O'M., Ed., Modern Aspects of Electrochemistry, Vol. 1, p. 243. London: Butterworths, 1954.

3. Bockris, J. O'M., "On Methods for the Large-Scale Production of Hydrogen From Water," in Veziroglu, T.N., Ed., Hydrogen Energy, Pt. A, p. 391. New York: Plenum Press, 1975.

4. Cox, K. E., Hydrogen Energy, a Bibliography With Abstracts. Alberquerque: University of New Mexico, 1974.

5. Engelhardt, V., Electrolysis of Water. Easton, Pa.: Chemical Publishing Co., 1904.

6. Escher, W.J.D. and Hanson, J. A., "Ocean-Based, Solar-to-Hydrogen Energy Conversion Macrosystem," in Veziroglu, T.N., Ed., Hydrogen Energy, Pt. A, p. 209-29. New York: Plenum Press, 1975.

7. Gregory, D. P., A Hydrogen-Energy System. Chicago: American Gas Association, 1972.

8. Juda, W. and Moulton, D. M., Chem. Eng. Prog. Symp. Ser., 59 (1972).

9. Kuhn, A. T., "Chlor-Alkali Industry," in Kuhn, A.T., Ed., Industrial Electrochemical Processes, p. 108. Amsterdam: Elsevier, 1971.

10. Salzano, F. J., "Hydrogen Storage and Production in Utility Systems," Third Q. Prog. Rep., Upton, N.Y.: Brookhaven National Laboratories, September 1974.

11. Smith, D. H., "Industrial Water Electrolysis," in Kuhn, A.T., Ed., Industrial Electrochemical Processes, pp. 127-57. Amsterdam: Elsevier, 1971.

12. Smith, D. H., "Water Electrolysis at Elevated Pressure." Paper presented at the Conference on the Electrolytic Production of Hydrogen, Faraday Division of the Chemical Society and Society of Chemical Industry, London, February 25-26, 1975.

13. Spacil, H. S. and Tedmon, C. S., Jr., "Electrochemical Dissociation of Water Vapor in Solid-Oxide Electrolyte Cells," J. Electrochem. Soc. 116, 1618-33 (1969).

14. Taylor, H. S., Industrial Hydrogen. New York: Chemical Catalog Co., 1921.

15. Tseung, A. C. C., private communication of May 1975.

16. Tseung, A. C. C. and Vassie, P. R., "The Evolution of Oxygen and the Role of Semiconducting Oxide Electrodes." Paper presented at the Conference on the Electrolytic Production of Hydrogen, Faraday Division of the Chemical Society and Society of Chemical Industry, London, February 25-26, 1975.

17. Veziroglu, T. N., "Hydrogen Energy Fundamentals, a Symposium-Course," Miami Beach, March 3-5, 1975.

18. Veziroglu, T. N., Hydrogen Energy, Pt. A and B. New York: Plenum Press, 1975.

19. Weisbart, J. and Smart, W. H., "Development of a CO_2-H_2O Solid-Oxide-Electrolyte Electrolysis System," Third Annu. Rep., Contract NAS2-4843. Sunnyvale, California: Applied Electrochemistry, Inc., 1970.

11. THE TRANSMISSION, STORAGE, AND DISTRIBUTION OF HYDROGEN — A. J. Konopka, J. B. Pangborn, and W. J. D. Escher

Hydrogen Transmission

It appears that small nuclear-power generators for individual customer use or even for substation use will not be commercially feasible. If the smallest economical generator size is a few hundred megawatts, waste-heat removal becomes a local problem, limiting the location of a power plant to specific areas. Because the preferred sites for such nuclear plants are near large bodies of water and most of the cooling water near load centers is already claimed, future energy-production sites will likely be large and remote.

Energy-production centers not near load centers must transmit the product energy from the concentrated production site to the centralized utilization site. Therefore, if hydrogen is to be used in large quantities, it will have to be transported in bulk, as are electricity and natural gas. One of the cheapest ways of moving energy, whether liquid or gas, is by pipeline. Because most long-distance pipelines are below ground, they do not have the disadvantage of being unsightly, as do high-voltage lines.

Transmission of hydrogen by underground pipelines can be compared with natural gas and electricity transmission over long distances. Generally, on an energy-delivered basis, natural gas will be the cheapest of the three to transmit; hydrogen will be intermediate in cost; and electricity will be the most expensive. It is evident that, because of the lower heating value of hydrogen (325 Btu/SCF) compared with that of natural gas (1050 Btu/SCF), approximately three times more hydrogen than natural gas must be transported to achieve an equivalent pipeline-energy-delivery rate.

Hydrogen is transmitted by pipeline in various parts of the world. However, compared with natural gas transmission, the distances are relatively short; and the energy flows are small. Because of economic and technical factors, the long-distance transmission of hydrogen could require the use of new, high-capacity compressors and drivers, as well as new pipeline materials. Compressors must be able to handle hydrogen's high diffusivity property (i.e., its tendency to leak), which may cause compressor-casing and valve-sealing problems.

The effect of hydrogen on pipeline components must be evaluated from a material-design viewpoint. Little is known about the effects of hydrogen on pipeline steels at high operating pressures. High operating pressures may cause "hydrogen embrittlement" of pipeline steel. Also, large compressors for pipelines may be constructed of materials that are susceptible to hydrogen attack. Undoubtedly pipelines can be constructed for hydrogen transmission; however, in order to keep transmission costs at a minimum, pipeline components that are both technically sound and economical must be developed. Because experience with hydrogen pipelining is not as extensive as that with natural gas systems, optimum-performance and minimum-cost pipeline components are not currently available.

Several research groups have studied the technological and economic aspects of large-volume, gaseous-hydrogen transmission. These studies are summarized below.

IGT Pipeline Optimization Study

The Institute of Gas Technology has conducted a pipeline optimization study of gaseous-hydrogen transmission.[18] The specific objectives were to determine a) which pipeline components are available and which would have to be developed for hydrogen transmission, and b) the best pipeline operating conditions for transporting certain quantities of energy in the form of gaseous hydrogen.

Pipeline Components

The results show that the availability of suitable compressors and drive engines for use in hydrogen transmission is questionable.

Turbocompressors and Drivers

Turbocompressors have been designed and are currently operational for high throughputs of hydrogen gas, but such high-throughput devices have never been designed to function at high operating pressures. In most instances, only a thicker casing is necessary.

The factor limiting the use of a radial turbocompressor with hydrogen is the pressure ratio achievable in one stage. This type of machine converts kinetic energy into a pressure head, and the pressure ratio is directly proportional to the rotor tip speed and is dependent on a) the physical properties of the gas and b) the rotor and diffuser geometry. For low-molecular-weight hydrogen,

achievable pressure ratios are far lower than those obtainable with natural gas at the same tip speed. The maximum tip speed is limited by the mechanical properties of the rotor.

In the IGT study, it was assumed that hydrogen-fueled gas turbine drivers power the turbocompressors. Current technology makes possible the use, with pipelines, of a directly connected, aircraft-type gas turbine with a turbocompressor.

In the 1950's, researchers at Pratt & Whitney (Div. United Aircraft Corp.) did considerable work on hydrogen-fueled, aircraft-type gas turbines. They successfully modified a J-57 engine for operation on hydrogen fuel and designed, constructed, and tested a special engine specifically designed for use with hydrogen fuel. Excellent results were obtained, but the program was abandoned before 1960. Hydrogen-operated gas turbines have higher efficiencies than corresponding units operating on conventional fuels.

Reciprocating Compressors and Drivers

Reciprocating compressors could be used with hydrogen pipelines. Many reciprocating-compressor installations are now handling hydrogen under various conditions of pressure, temperature, water-vapor content, and corrosivity. Compression cylinders would have to be quite large to be able to transport pipeline quantities of gaseous hydrogen. Worthington CEI has made gas compression cylinders with a 19-inch stroke and a bore as large as 42 inches. A need for reciprocating-compressor development is not anticipated, because large cylinder compressors are available that don't sacrifice the possibility of maintaining a high pressure ratio for each compression stage. Worthington stated that compressors designed for use with hydrogen need only special steel piston rods and Teflon rings to surmount hydrogen-embrittlement problems.

The problem involved in using such a compressor with hydrogen pipelines would be obtaining a driver of sufficient speed and power. Although considerable success has been achieved in converting small, automobile-type piston engines to hydrogen use, a separate research program would be necessary to achieve an optimum scale-up to large engine size.

Other Compressors

Screw compressors have not been used in very-high-pressure applications (above about 600 psia). However, they combine the valuable features of both positive-displacement and dynamic machines and are "oil free." If developed for higher pressure applications, they could be valuable for use with hydrogen pipelines.

Axial turbocompressors under development are expected to be highly efficient machines comparable to reciprocating machines. The resulting price per unit of horsepower should approximate the radial-turbocompressor price currently quoted by Elliott Co.

In the IGT study, radial-turbocompressor and turbine-driver technical and economic data were assumed because the gas industry tends to use turbocompressors for high-throughput gas flows.

Reciprocating devices have higher capital and installation costs, in $/hp, than turbomachinery. However, reciprocating compressors provide a higher fuel efficiency for long-term operation. Currently, the break-even point for operating turbomachinery and reciprocating devices is 10 years. Turbomachinery is relatively new, and improvements may be forthcoming.

Initial Compressor

A hydrogen-transmission pipeline is expected to operate at some average pressure between 750 and 2000 psia. If hydrogen is not manufactured at this pressure, an initial compression step (employing an initial compressor) will be necessary to bring the gas up to pipeline pressure. (Pipeline compressors, which compress the gas flowing through the pipelines to compensate for pressure losses, have a much lower ratio of inlet to outlet pressure than initial compressors.) Because many electrolyzers and many thermochemical hydrogen-production processes now under investigation operate at modest pressures, it is important to consider the cost factors and technological capabilities involved in this initial compression step.

According to representatives of the Elliott Co., a manufacturer of turbocompressors, the use of an initial compressor could present a major developmental problem for turbomachinery — especially if hydrogen cannot be produced at an elevated pressure. Only a 1.4:1 pressure ratio is attainable per casing with turbocompressors. Therefore, if hydrogen is produced at

atmospheric pressure, a great number of compressor casings would have to be placed in series to attain the pressures used in pipeline transport. However, if the hydrogen could be produced at 750 psia, for example, it could be put directly into the pipeline or be boosted by turbocompressors to higher pressures. (Hydrogen produced at 750 psia would need only two compressor casings, in series, to reach 1500-psia pipeline operating conditions.) Also, intercoolers must be added to multistage compressors to remove the heat of compression.

Reciprocating compressors (positive-displacement machines) achieve a much greater pressure ratio, so initial compression is less of a problem. For example, 17,000 SCF of hydrogen per minute can be compressed from atmospheric pressure to 750 psia in four stages. However, at pipeline conditions this represents only 340 CF/min. For long-distance hydrogen transmission to be economical, the capacity of these machines will have to be greatly increased, at least by a factor of 20.

Combinations of turbocompressors to handle flow and reciprocating machines to provide compression should be considered as possible economical solutions to the problem presented by the need for a large-volume initial compressor for use with hydrogen.

Optimum Operating Conditions

A computer program was employed in this study to determine the economic characteristics of a hydrogen-transmission system. Given the design throughput (flow of gas), overall transmission distance, and thermodynamic and geographical conditions, the program calculated the minimum transmission cost by –

a. Optimizing the compression section
b. Finding the optimal combination of all the optimized sections.

Figure 11-1 is a schematic view of the system of variables used for IGT's study of pipeline-section optimization.

The cost trends of hydrogen transmission were calculated including the effect of hydrogen-volume throughput in a single pipeline of varying diameters (24, 30, 36, 42, and 48 inches). Various hydrogen-fuel-production costs (from $2 to $4/million Btu), were assumed; and average operating pressures of 750, 1000, 1500, and 2000 psia were considered.

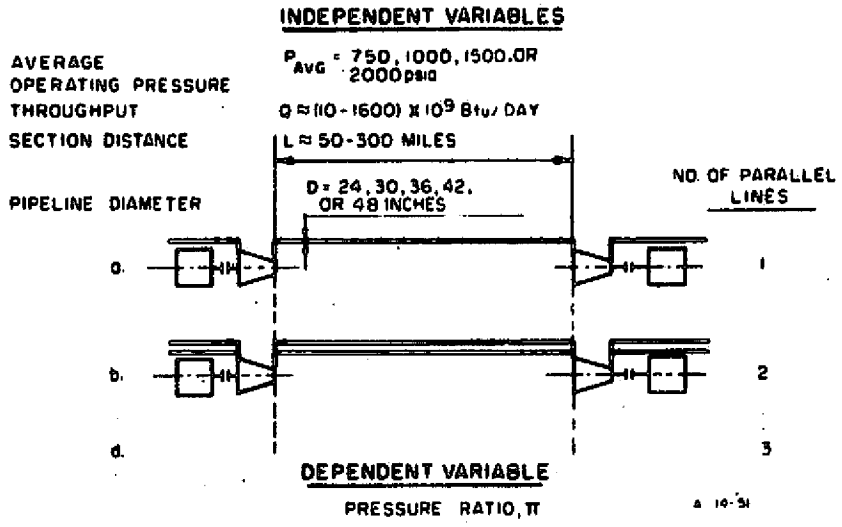

Figure 11-1. IGT SYSTEM OF VARIABLES USED TO OPTIMIZE A COMPRESSION SECTION OF GAS-TRANSMISSION LINE

The following conclusions were reached in the IGT study:

- For 24 and 30-inch pipe, operating at higher average pressures (1500 and 2000 psia) results in a major decrease in hydrogen-transmission cost.
- For 24 to 30-inch single-line pipes operating at full capacity, hydrogen-transmission cost increases markedly with compressor-section spacing length at low average pressures (750 psia).
- For pipes of larger diameter, an insignificant decrease in transmission cost is obtained by operating at a higher average pressure.
- For 48-inch-diameter and some 42-inch-diameter pipelines, hydrogen-transmission costs actually begin to increase with operation at 2000 psia. Therefore, cheapest pipeline operation is at a pressure somewhere between 1500 and 2000 psia.
- No great advantage is apparent for operation with very-long-distance compressor pipe sections (i.e., with long distances between compressors). A combination of shorter sections (i.e., closer compressor-station spacing) at a specific diameter may be used at no apparent increase in cost.

Figure 11-2 is a comparison of transmission costs for hydrogen and natural gas at optimized conditions. In completely optimized systems, the cost of hydrogen transmission (at an average operating pressure of 750 psia) will be between 3.5¢ and 5.5¢/million Btu-100 miles. This is 2 to 3 times more than today's natural-gas-transmission costs.

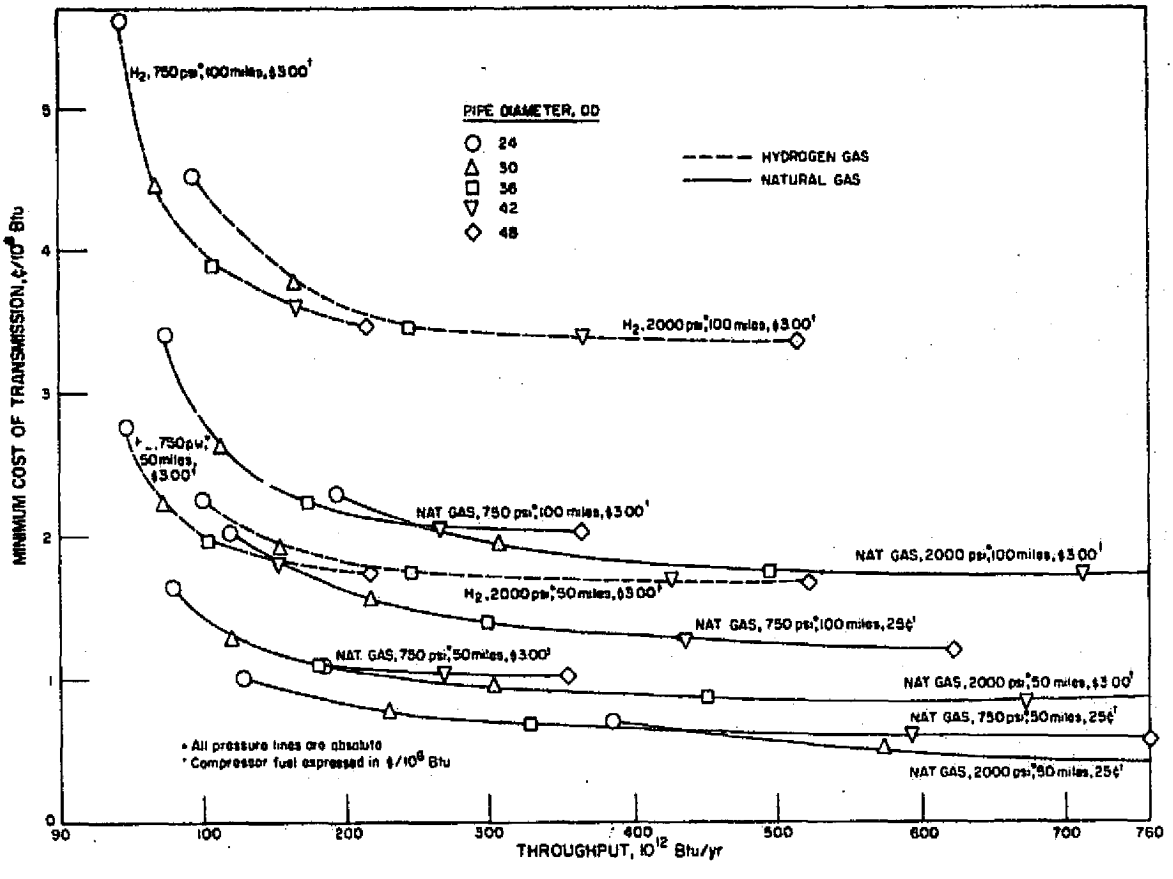

Figure 11-2. OPTIMIZED TRANSMISSION COSTS FOR HYDROGEN COMPARED WITH NATURAL GAS

Figure 11-3 is a plot of gas-transmission costs for 1000 miles (in ¢/million Btu) versus compression-section spacing that was made to determine the effect of the distance between compression stations on gas-transmission cost. Apparently there is little cost advantage in operating hydrogen lines with longer distances between intermediate compressors; however, certain cases pictured do show a slight reduction in cost with longer intermediate-compressor-station spacings.

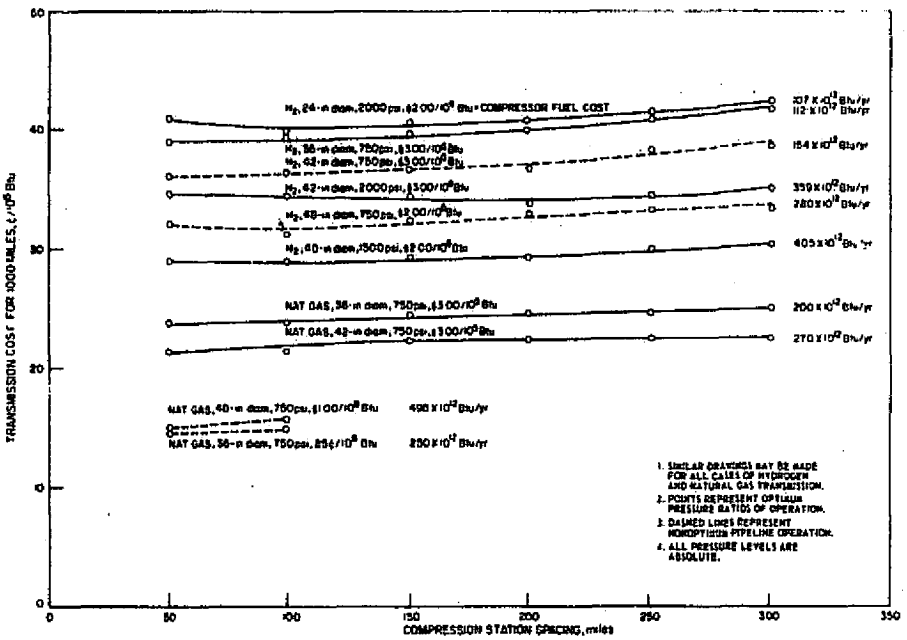

Figure 11-3. 1000-MILE TRANSMISSION COST COMPARISON FOR HYDROGEN AND NATURAL GAS WITH DIFFERENT INTERMEDIATE COMPRESSOR SPACINGS

EURATOM

EURATOM, in Italy, has conducted a study to determine the economic characteristics of transporting hydrogen, natural gas, and oxygen by an optimized pipeline network.[3] Specifically, given a design throughput, overall transmission distance, and thermodynamic and geographical conditions, the minimum transmission cost was calculated by optimizing the number of compression stations for an optimal pipeline diameter.[12] When used in an analytical form, this calculation determines the number of compression stations that result in the minimum cost of transporting a given heating value over a certain distance.[12] The minimum cost, therefore, is a function of the throughput and of the overall distance, and the resulting optimum pressure ratio, pipe diameter, and station spacing are shown as a single value. Apparently, for this study it was assumed that gas compressors would be powered by electric motors. Thus compressor-fuel costs in this study are the same for both hydrogen and natural gas.

The EURATOM report concludes that hydrogen is 30% to 50% more expensive to transport by pipeline than natural gas. Data for comparison of transmission costs for natural gas (assumed here to be methane) and hydrogen, at an operating pressure of 1280 psi, are shown in Table 11-1. The ratio of costs increases with an increase in distance and slowly decreases with an increase in throughput. It is obvious from Table 11-1 that the optimum distance between intermediate compression stations is greater for hydrogen than for methane. Similar results have also been reported at other pipeline working pressures. Pipeline investment costs (for construction of the pipeline) were also reported to be about 45% to 60% higher for hydrogen than for natural gas because of the larger diameter pipelines used with hydrogen.

EURATOM has found that an increase in pipeline operating pressures reduces the transmission cost for hydrogen, as shown in Table 11-1 for a given throughput of 250 trillion Btu/yr and a transmission distance of 621 miles. The costs shown in Table 11-1 do not take initial gas compression into account. However, EURATOM did report the effect of initial gas compression on transmission costs for both methane and hydrogen, and the findings are shown in Table 11-2. The inlet pressure is 10 kg/sq cm (142 psi), transportation pressure is 90 kg/sq cm (1280 psi), and the throughput is 125 trillion Btu/yr.

It is clear that initial compression is an important factor in the total cost, especially for short distances. Also, the impact of initial compression on total costs is greater, in absolute value and in percentage, for hydrogen than for methane.

General Electric Co. (Tempo), Calif.

R. A. Reynolds and W. L. Slager of GE have developed an analytical model for developing characteristics and costs of delivering gaseous and liquid fuels by pipeline.[23] Given the desired energy-flow rates, certain other inputs, and an initial estimate of pipe size, the model computes the first cost of the installed line and determines its required compressor stations. The procedure involves systematic variations in pipe diameter for identification of the minimum-cost configuration. Once determined, the energy-transport cost is calculated, taking into account system amortization and the fuel required to operate the line.

Table 11-1. COMPARISON OF COSTS FOR HYDROGEN AND METHANE, ACCORDING TO EURATOM[3]

Throughput, Gcal/s (10^6 Btu/yr)	Distance, (km) miles	Number of Sections		Distance Between Stations, miles		Minimum Cost, $/10^6 Btu		Hydrogen/Methane Transmission Costs	Hydrogen/Methane Capital Costs	Compression Ratio	
		Hydrogen	Methane	Hydrogen	Methane	Hydrogen	Methane			Hydrogen	Methane
1, 125	(1000) 621	2	5	311	124	0.29	0.20	1.40	1.46	1.541	1.407
2, 250	(1000) 621	2	6	311	104	0.23	0.16	1.41	1.46	1.447	1.274
3, 375	(1000) 621	1	5	621	124	0.19	0.14	1.38	1.61	1.500	1.298
4, 500	(1000) 621	1	5	621	124	0.17	0.13	1.36	1.58	1.500	1.274
1, 125	(2000) 1243	8	13	155	96	0.61	0.41	1.46	1.48	1.192	1.288
2, 250	(2000) 1243	7	15	177	83	0.48	0.33	1.48	1.51	1.180	1.204
3, 375	(2000) 1243	2	16	621	78	0.42	0.28	1.48	1.59	1.737	1.169
4, 500	(2000) 1243	2	16	621	78	0.38	0.26	1.48	1.59	1.683	1.156
2.5, 62.5	(500) 311	1	2	311	155	0.16	0.12	1.31	1.43	1.500	1.829

Pressure in the pipe is assumed to be 90 kg/sq cm.

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Table 11-2. EFFECT OF INITIAL GAS COMPRESSION ON TRANSMISSION COSTS (EURATOM STUDY)

Gas	Distance, miles (km)	Total Transportation Cost, ¢/10^6 Btu	Initial Compression As Percentage of Total Cost, %
Methane	311 (500)	16	38
	621 (1000)	25	23
	932 (1500)	36	16
	1242 (2000)	47	13
Hydrogen	311 (500)	36	54
	621 (1000)	52	46
	932 (1500)	68	35
	1242 (2000)	84	29

In a properly designed system, the cost of transmitting hydrogen by pipeline is from 30% to 50% higher than for an equal amount (in terms of energy) of natural gas. This conclusion is based on pipelines constructed to be used under conditions representative of those in the Midwestern United States. If higher installation costs were used for both gases (methane and hydrogen), the relative transmission costs would become similar, but the absolute figures would increase.

Reynolds and Slager conclude that increased pipe diameter is the primary reason for hydrogen being more costly to transport than methane. An increase of from 25% to 50% in pipe diameter is reflected directly in the required capital costs, of which from 75% to 80% is attributed to the cost of pipe and installation and the remainder is for compressor facilities. Optimum compression ratios at compressor stations were found to be lower for hydrogen (1.1:1) than for natural gas (from 1.25:1 to 1.30:1). Compressor-station spacings of from 50 to 75 miles were related to these operating-pressure ratios.

To calculate gas-transmission costs, a compressor-engine-fuel cost of 40 ¢/million Btu has been assumed for both hydrogen and natural gas. This factor (primarily) accounts for the difference in transmission costs predicted by the GE and IGT studies. Reynolds and Slager also studied the effect of transporting cooled hydrogen gas by pipeline. They found that for temperatures from ambient to -300 °F, the optimized pipeline design requires between one and two times the compressor power of the nominal case. If an insulated

pipe were assumed to be required, as would actually be the case, pipelining of hydrogen would prove to be more expensive at reduced temperatures. Therefore they have concluded that the refrigeration of hydrogen gas is not desirable.

G. G. Leeth of GE also conducted a study comparing hydrogen-transmission costs with those of other energy-transmission systems.[20] The systems studied included energy transmitted in the form of electricity (underground and overhead), hot water, chemical heat (EVA-ADAM),* hydrogen and oxygen, hydrogen (solely), oxygen (solely), and methane.

This preliminary study of energy transmission showed that for nonfossil-fueled energy centers, hydrogen is superior to the other energy-transport modes considered. An EVA-ADAM system is intermediate in cost between hydrogen and electricity. The hot-water system is slightly more expensive than overhead electricity transmission.

National Bureau of Standards

C. F. Sindt has conducted a study to determine the most economical method for delivering liquid hydrogen.[13] From economic considerations, alone, it was concluded that hydrogen should not be liquefied for transmission or transport, except when delivery is across an ocean or when the hydrogen is to be used as a liquid. However when liquid hydrogen is required, the costs of transmission, production, and liquefaction must all be considered before the most economical method of delivering the liquid hydrogen can be determined.

Sindt assumed that hydrogen could be produced by electrolysis, using power generated by a large electrical power plant. Various schemes were considered for delivering liquid hydrogen to users at distances of 50 and 100 miles.

Conclusions from this study indicate that for current electricity bus-bar costs, the most practical means for supplying liquid hydrogen to users within

* Heat from a nuclear reactor is used to provide the endothermic energy for a chemical reaction ($CH_4 + H_2O \rightleftharpoons 3H_2 + CO$). The products are then pipelined to a number of chemical reactors (close to the customers' premises) where the chemical reaction is reversed and the heat of reaction recovered. The products of this second reaction are pipelined back to the power station where they provide feedstock for the first reaction.

about 60 miles is by truck. This method of transport is versatile because trucks can deliver liquid hydrogen to many different users. If the use is at a single installation, such as an airport, a gas pipeline with a parallel power line (to run the liquefier) is the best choice. Such a system has the added advantage of situating the liquefier so that any boil-off gases from storage, transfer, or detanking operations can be recovered and reliquefied.

For longer distances, from 600 to 1200 miles, railroad delivery of liquid hydrogen is attractive. As is the case with trucks in short hauls, railroads are versatile because two or more large users at a great distance from each other can be supplied with very little additional cost. Again, if all use is confined to a single installation or if all the users are close to a large storage dewar, a gas pipeline with a parallel electric-power line looks to be most efficient and practical. In this case, the liquefier is located so that boil-off gas from heat leaks or liquid transfer can be reliquefied. For transoceanic hydrogen transmission, liquefaction and shipping is most attractive.

Central Electricity Generating Board (CEGB), England

The total costs of gaseous hydrogen, methanol, and electricity transmission have been compared in a study by CEGB.[11] Also included in this study is a comparison of the relative costs of making electricity and electrolytic hydrogen in a base-load plant, transmitting them over 125 miles, and distributing them. (See Table 11-3.) These figures indicate that electrolytic hydrogen is much more expensive to manufacture, transport, and distribut than is electricity. CEGB concludes that development of a successful thermochemical process could reverse this situation.

CEGB, after calculating transmission costs as a function of transmission distances, has determined the break-even distances, shown in Table 11-4, above which it would be cheaper to transport nuclear energy as electrolytic hydrogen than as electricity.

According to CEGB's study, the transmission cost of hydrogen gas is approximately 7 ¢/million Btu for 200 km, and the cost of 765 kV ac of overhead electricity is 12¢/million Btu for 200 km. However over realistic distances, the total delivered cost of electrolytically produced hydrogen is not less than the cost of transmitting nuclear energy as electricity.

Table 11-3. ENERGY-TRANSMISSION STUDY BY THE CENTRAL ELECTRICITY GENERATING BOARD, ENGLAND[11]

	Manufacturing Efficiency, %	Manufacturing Cost, $/10^6 Btu	Transmission Cost for 200 km, $/10^6 Btu	Subtotal Cost of Energy Transmitted 200 km, $10^6 Btu	Conversion and Distribution Cost, $/10^6 Btu	Total Cost Distributed Energy, $/10^6 Btu
Electrolytic Hydrogen (Distributed as Gas)	24-28	6.33	0.07	6.40	1.49	7.89
Electrolytic Hydrogen (Distributed as Electricity)	12-14	12.65	0.15	12.80	3.87	16.67
Electricity						
400 kVAC (Overhead)	33-40	3.79	0.20	3.99	1.98	5.97
765 kVAC (Overhead)	33-40	3.79	0.12	3.91	1.98	5.89
DC (Overhead)	33-40	3.79	0.55	4.34	1.98	6.32
DC (Underground)	33-40	3.79	0.67	4.46	1.98	6.44

Table 11-4. BREAK-EVEN ENERGY-TRANSPORT DISTANCES

Form of Electric Transmission	Generation and Transmission Only	Generation, Transmission, and Distribution as a Chemical Fuel	Generation, Transmission, and Distribution as Electricity
	miles (km)		
ac 400 kV	4780 (7700)	3,800 (6,100)	Never
ac 765 kV	4780 (7700)	38,500 (62,000)	Never
dc (Underground)	1680 (2700)	1,240 (2,000)	14,300 (23,000)

American Electric Power Service Corp.

C. A. Falcone has conducted a study[4] comparing the efficiency of a system in which electricity is converted (by electrolyzers) to hydrogen, which is transmitted and reconverted to electricity by a fuel cell, with the efficiency of an all-electric system. He shows that the energy-conversion losses in a hydrogen-transmission system would result in a much higher total-energy consumption and would necessitate greater power-plant capacity for the same level of delivered usable energy. Utilization of this mixed system would require about 2-1/2 times as much primary fuel as a purely electrical production and transmission system. Also, the hydrogen-electric system would require about 1.7 times as much plant capacity.

Falcone mentions that improvements in electrolytic hydrogen-production methods and fuel-cell technology could lower the primary-energy consumption. Also, development of a highly efficient thermochemical hydrogen-production method could significantly increase the efficiency of the conversion from primary energy to hydrogen. The study points out that if hydrogen were the preferred fuel for certain end uses in which electricity is unsuitable, the efficiency issue would be purely academic.

Stevens Institute of Technology

J. G. Hollenberg has completed a study determining the availability and desired characteristics for compressors for use in hydrogen transmission.[12] In general, before selecting a compressor for a certain application, one must determine the performance requirements. These requirements include operating-pressure ratios, efficiencies, flow rates, and special characteristics such as pulsations, possible contamination of the gas by lubricants, life time, and maintenance.

Currently two types of compressors are available for use with hydrogen: older, reciprocating machines driven by gas-fueled engines and centrifugal turbocompressors driven by gas turbines. Although centrifugal compressors may have some more desirable operating characteristics than reciprocating machines, the capability of producing high pressure ratios is not associated with turbomachinery, unless extensive multistaging is considered. Because of hydrogen's rapid diffusivity, there may be sealing problems with the reciprocating machine. The centrifugal compressor has recently replaced the reciprocating compressor in many installations because of its increased capacity, steady operating conditions, and lower initial cost and maintenance expenses.

According to Hollenberg, a third type of compressor, considered to have merit for use in hydrogen transmission, is the regenerative compressor. This compressor is capable of producing a dynamic pressure head that would require seven or eight stages for production in a centrifugal compressor. Use of the regenerative compressors has been limited because of their low specific speed and low operating efficiency (50%) in low speed regimes. Even at very low speeds, the regenerative compressor is more efficient than the centrifugal compressor. Although much work has been done on the regenerative compressor since World War I, compressors of this type over 50 hp have never been developed.

University of California, San Diego

L. Icerman has conducted a study comparing the relative costs of transmitting energy as hydrogen, natural gas, and electricity.[15] The transmission cost for each was broken down into three components: capital cost, operating cost, and annual operating cost (which includes investment, depreciation, and taxes). According to Icerman, the cost of energy transmission is dependent upon two parameters: pipeline cost and compressor-fuel cost. For example, pipeline costs for natural gas constitute from 70% to 90% of the total construction cost.

In Icerman's analysis, 30 and 36-inch diameter pipes were investigated for equivalent energy throughputs of natural gas and hydrogen at a fixed transmission distance and pressure. Although a 36-inch-diameter pipeline has a higher tonnage and consequently a higher initial cost, its horsepower requirement is considerably less. Thus, the capital and operating costs

are less and result in an overall cost 13% lower for the 36-inch-diameter pipeline than for the 30-inch-diameter pipeline.

Assuming that a hydrogen pipeline delivers the same amount of energy as a natural gas pipeline, results indicate that, because of hydrogen's lower volumetric heating, 3.2 times as much hydrogen (by volume) must be moved to equal the volumetric content of natural gas. At 750 psia, the different compressibility factors for hydrogen and natural gas result in an increase in the natural gas-to-hydrogen volumetric-heating-value ratio to about 3.8:1. Compressor-fuel costs for the natural gas system account for only 2% of the total operating cost. In the hydrogen system, it accounts for 41%. The huge gas-volume-flow requirement of hydrogen (compared with natural gas) was reflected in hydrogen's high horsepower requirement (550% that of natural gas). Icerman noted that as the pipe diameter increases, resulting in lessened horsepower requirements for both natural gas and hydrogen, the ratio of hydrogen tc natural gas operating costs declines.

In the comparison of hydrogen-transmission cost with that of electricity transmission, both underground cable and overhead lines were considered. The cost of hydrogen transmission is from 10% to 60% (for 700kV and 200kV ac, respectively) less than long-distance overhead electricity transmission. Comparison of underground-cable electricity transmission with overhead transmission indicates that underground transmission is from 10% to 20% more expensive than overhead transmission. In the future, the cost of electric-energy transmission may be as high as 25 times the cost of hydrogen transmission (at an equal energy-delivery rate).

Discussion of Transmission Studies

Hydrogen-transmission studies have generally included economic and technological assessments of present capabilities to transport pipeline hydrogen. The cost of transmitting hydrogen 100 miles in underground pipelines is approximately 1.4 to 1.6 times that of an equivalent energy capacity of natural gas transmitted by underground pipeline, if compressor-fuel costs of both fuels are considered to be the same (e.g., if both compressors are electrically driven).[3,23] Electrically driven compressors have been used in transmission systems, but recently intermediate pipeline compresso s on natural gas transmission lines were adapted to operate on natural gas. If natural gas were assumed to drive intermediate pipeline

compressors for pipeline gas transmission, the transmission cost of natural gas would be far lower, and the corresponding cost of transporting hydrogen in hydrogen-driven pipelines would be 2 to 3 times as great per 100 miles.[15,18]

Compressor and driver availability for hydrogen transmission is somewhat questionable.[12,18] Reciprocating compressors could be used with hydrogen pipelines. Many reciprocating-compressor installations are handling hydrogen under various conditions of pressure, temperature, water-vapor content, and corrosiveness. Compression cylinders would need to be quite large to transport pipeline quantities of gaseous hydrogen, but these large machines are currently available. One problem with using such a compressor for pipeline service is obtaining an engine driver that would attain sufficient power and rpm.

Currently operational turbocompressors that are designed for high throughputs of gas have never been utilized in operations involving high operating pressures. Hydrogen-fueled gas turbine drivers could be used to power centrifugal compressors; however, the technology involved is currently unproved for industrial applications. Other types of newer compressors — including axial, regenerative, and screw compressors — could be used in hydrogen transmission, as long as developmental research is undertaken.

When electricity-transmission cost is compared with the cost of pipeline transmission of natural gas or hydrogen, pipeline transmission is seen to be much cheaper (on an energy-delivered basis). Depending on the type of transmission considered, electricity may be from 5 to 20 times more costly to transmit than natural gas (for an equivalent amount of heat energy).[15,18]

Because transmission of hydrogen gas is expected (from calculations) to be cheaper than electricity transmission, the production of hydrogen from water, along with subsequent transmission, could be an economical alternative to the more costly electricity transmission associated with the nuclear era. It has been suggested that as transmission distances increase, pipeline transmission of gaseous fuel will be vastly more economical than electricity transmission.

If a customer requires electrical energy, however, transmitting the energy in the form of hydrogen and reconverting it to electricity results in large energy-conversion efficiency penalties, which result in much additional cost.[4,11] This increased cost is a direct reflection of increased capital costs for nuclear capacity. However, if the delivered hydrogen could be used directly as a fuel, the overall system efficiencies would probably be more attractive. As shown in Table 11-5,[27] production of hydrogen by electrolysis could result in an energy system less efficient than electricity. However, if space or industrial heating is desired rather than work (electricity) and/or if thermochemical methods of hydrogen production could be implemented, then an energy system that used hydrogen as its transmittable energy form would have a great deal of merit.

Table 11-5. COMPARISON OF ENERGY-SYSTEM EFFICIENCIES[27]

Future System	Nuclear Heat to fuel	Transmission, Storage, and Distribution	End Use	System Efficiency
	% Efficiency			
Hydrogen (95% Eff. Electrolyzer)	42.8	95	70 (Flame) 84 (Catalytic)	29 34
Electricity	45	90*	95	38
Hydrogen (Thermo-chemical)	55	95	70 (Flame) 84 (Catalytic)	37 44

* Estimate of transmisson and distribution efficiency.

Hydrogen Embrittlement

One of the major requirements for the handling, storage, and transmission of hydrogen is a material that will not be susceptible to severe degradation of its mechanical properties by atomic and molecular hydrogen. Because hydrogen readily diffuses into most structural materials, embrittlement is a serious factor that must be considered in designing for the containment of gaseous hydrogen. Materials for construction of compressors, pipelines, and storage vessels must be tested to determine whether or not they are suitable for use with hydrogen. For example, failures because of embrittlement in gas pressure vessels have occurred at as little as one-tenth of design pressure.[13]

Although the degradation of metals by hydrogen has been recognized in the failure of certain structures, the specific mechanism involved is not clearly understood. Currently, three explanations for the problem are proposed:

1. Hydrogen-reaction embrittlement
2. Internal hydrogen embrittlement
3. Hydrogen-environment embrittlement.

Hydrogen-reaction embrittlement is a result of the chemical reaction of hydrogen with a metal or some alloy. Some examples of hydrogen-reaction embrittlement are the formation of irreversible hydrides of titanium, niobium, zirconium, and tantalum; the decarburization of steels; and the formation of high-pressure water bubbles and methane in metal voids.

Both internal and environmental hydrogen embrittlement result from hydrogen atoms dissolving in the metal. Any hydrogen-containing chemical solution can cause internal hydrogen embrittlement. This problem is often encountered in metal- or petrochemical-processing facilities. Hydrogen-environment embrittlement is the degradation of mechanical properties resulting from the adsorption of hydrogen on the surface of a metal. This type of embrittlement manifests when a crack begins to form in a metal in the presence of hydrogen.

The degree of hydrogen embrittlement depends on the following:

a. The metal and its constituents, along with its microstructure
b. The applied stress and impurities present in the hydrogen environment.

The rate of strain is a parameter important in determining the degree of embrittlement. Low strain rates promote maximum embrittlement, allowing hydrogen transport near the crack tip. Metals conditioned for high strength are often more susceptible to embrittlement than their lower strength counterparts.

The purity of the hydrogen environment can have profound effects on the degree of embrittlement. Small amounts of oxygen and some inert gases, in some instances, have totally eliminated the embrittling capability of hydrogen. Small additions of oxygen, suflur dioxide, carbon monoxide, and carbon disulfide are also effective embrittlement inhibitors. The effects of protective coatings have also been investigated. An effective coating must have a low permeability, must be nonporous, and must adhere well to the substrate.

Protective coatings do have potential benefits for use with hydrogen, but economics will be important in the final selection.

No evidence has been presented that indicates embrittlement problems with nonmetals, although little research has been performed in this area. Permeation through polymers, although much greater than through metals, is not expected to be a problem in plastic pipes.

Because hydrogen transportation and storage systems might operate at moderate pressures (1000 to 2000 psia), there will certainly still be situations in which a combination of moderate pressure, room temperature, and high-purity hydrogen will lead to the degradation of the proposed structural materials. A considerable amount of work has been done in the area of hydrogen embrittlement of structural materials.[30] However, work done to evaluate hydrogen-embrittlement problems for materials used in pipelines, storage facilities, and other areas of the hydrogen economy is somewhat limited.

Recent work performed by the Battelle Memorial Institute for IGT and the American Gas Association was to determine whether or not hydrogen embrittlement of pipeline materials would be a significant problem in a hydrogen-energy system.[5] It was shown that certain hydrogen-induced problems (hydrogen stress cracking, loss of metal ductility, and hydrogen-environment embrittlement) could be expected with the operation of a hydrogen pipeline. Few problems are anticipated in the bulk of the pipeline, whether it is made from current standard pipe steels or from a higher strength steel with a yield strength of from about 100,000 to 112,000 psi. The abovementioned problems would be associated with regions of the pipe that exhibit abnormal properties, such as hard spots (concentrations of high-strength material or hard-weld zones) and certain defects or other factors increasing stress (such as abrupt changes in section), or that are subjected to excessively high soil stresses. Problems may also be encountered with a few of the compressor parts that are made from higher strength steels.

Conclusions from results obtained by the Sandia Laboratories indicate that the hydrogen-embrittlement problems of proposed pipeline and storage structures may be surmounted by careful and costly design.[30] Economics will be a problem because the size of the facilities and quality control dictate the use of low-cost materials. With underground pipelines, the problems are compounded by corrosive attack, which leads to the initiation of cracks.

Therefore, improved structural materials for the storage of hydrogen as metal hydrides or cryogenic hydrogen are required so that design of the unit wil be economical.

Hydrogen Storage

A capacity for storage is needed in any energy-delivery system for two fundamental reasons: 1) to be able to reconcile the seasonal variations in demand with the economic requirements for a virtually steady rate of production and transmission and 2) to accommodate temporary interruptions in production and transmission and to compensate for the inability to make accurate short-term forecasts of demand. Storage systems are incorporated in all natural-gas-energy systems, and the same capability must be provided in a hydrogen-energy system. The specific type of storage selected will be determined by various local requirements and constraints. An important parameter in the selection of a storage type is volume or storage purpose (e.g., seasonal, daily, hourly, or security). Some background on natural-gas-storage systems is provided to show the types of systems that will be required for a hydrogen-energy system.

Storage of natural gas is required to compensate for variations in demand for energy between winter and summer. The degree of the "seasonal energy swing" depends on the difference between the amount of gas required for home and commercial heating and that required for nonwinter needs. For example, Consumers Power Co., serving the mid-Michigan area, reports a typical demand of 2.2 billion SCF/day in July and 16 billion SCF/day in December. This seasonal variation factor of approximately 7 is accommodated by dependence on depleted-field underground storage, in which gas from transmission lines is injected to storage during the nonheating periods of the year.

Most gas-distribution systems experience brief periods (from 1 to 3 days) of yearly maximum demand. Instead of sizing main sources of supply to accommodate daily peaks, it is more economical to introduce supplementary supplies that are stored near the load centers. A typical form of peakshaving used in the gas industry is provision of storage facilities for either natural gas (for example, as LNG) or propane, which is mixed with air to produce substitute natural gas. In addition, a small storage capacity exists within the transmission lines. This capacity, known as "linepack," becomes available by allowing the mean operating pressure of a pipeline to fluctuate during the periods of variable demand.

Methods of Hydrogen Storage

A number of methods exist for the storage of hydrogen, whether liquid or gas. Each of these will be treated in turn.

Metal-Hydride Hydrogen Storage

Hydrogen can be stored by chemically combining it with various metals and alloys to form hydrides.[33] Heat is released during the hydriding process. During the dehydriding process, the hydride is dissociated by heating, and hydrogen gas is released for use. Hydrogen storage densities equivalent to liquid-hydrogen densities can thus be obtained. At present, the main technical drawback of metal-hydride storage is the very high overall weight and volume involved. Other critical factors in a hydride system are enthalpy or heat of formation, equilibrium pressure (as a function of temperature), cost, abundance, physical form, rate of formation and dissociation, physical stability, tolerance to impurities, and safety.

Many pure metals and alloys (including lanthanum, samarium, and other rare-earth-metal alloys) are considered candidates for hydride formation. Current research is focused on the development of cheap metals or alloys, rather than on development of the generally expensive rare earth metals. Development of iron-titanium alloy (FeTi), which is a relatively inexpensive material, is under way.

The basic reaction in the hydriding of FeTi alloy, a representative alloy-hydriding system, is –

$$1.08\ FeTi\ H_{0.1} + H_2 \underset{\Delta Hf}{\overset{-\Delta Hf}{\rightleftharpoons}} 1.08\ FeTi\ H_{1.95}$$

The hydride decomposes readily at a pressure that is dependent upon alloy composition and temperature. Figure 11-4 illustrates this behavior in an FeTi system operating at 63°F.[23] A characteristic curve may be drawn for any hydride at any operating temperature.

The lower curve in Figure 11-4 represents the dissociation pressure for the reverse reaction; and, as shown, higher pressures are needed for

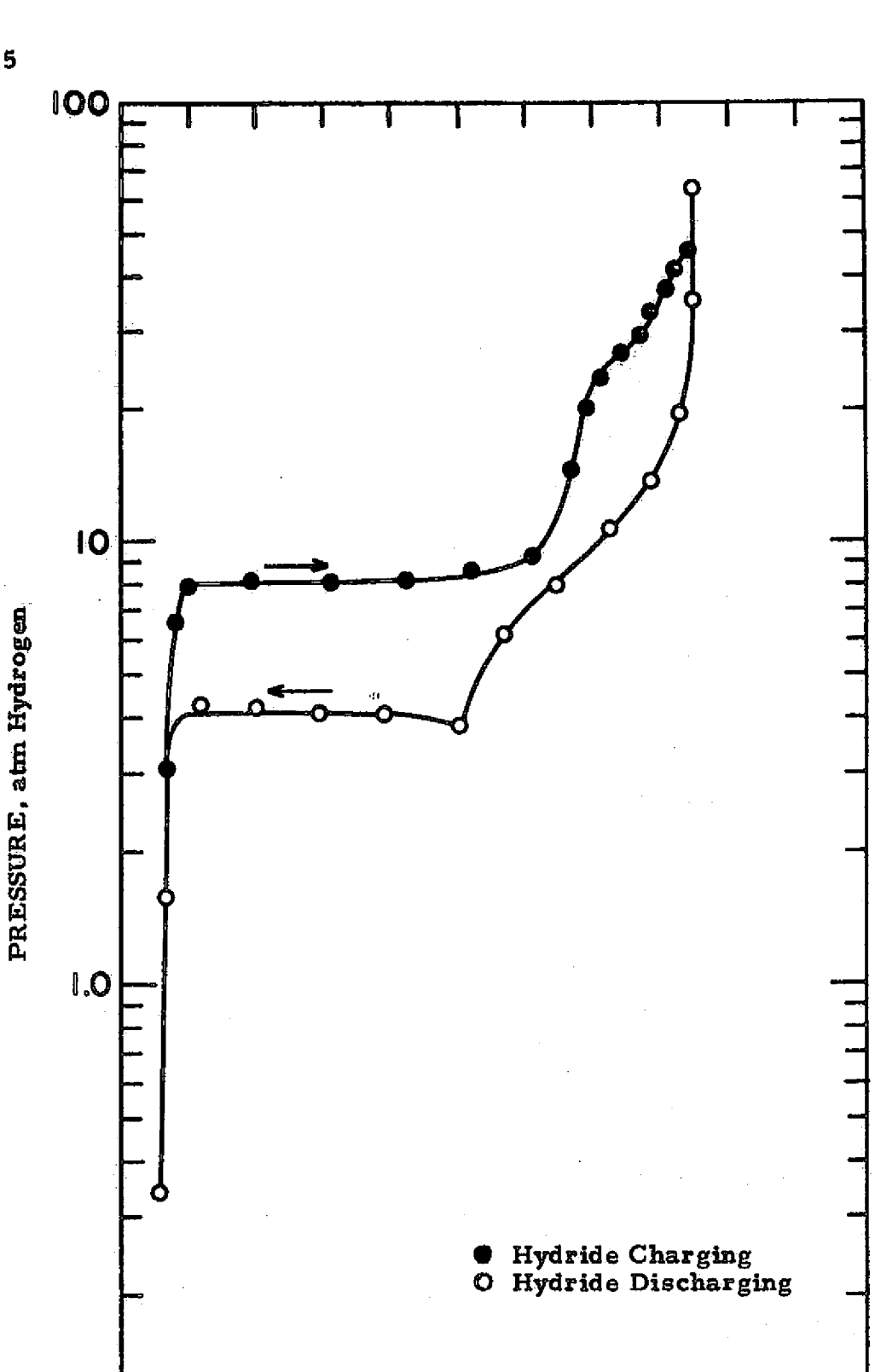

Figure 11-4. PRESSURE-COMPOSITION ISOTHERMS FOR AN $FeTiH_x$ SYSTEM[26]

the forward reaction. Impurities commonly present in commercially produced alloys can change the isotherm slope and may reduce the storage capacity of the hydride.[28]

Other candidates for metal-hydride hydrogen storage and their properties are shown in Table 11-6. These alloys are being studied at research laboratories around the world, as shown in Table 11-7.

Table 11-6. CANDIDATES FOR METAL-HYDRIDE STORAGE

Hydride Material	Heat of Formation, cal/mol	Grams of Hydrogen/Grams Metal, wt % Hydrogen	Effect of Other Gases (Water Vapor and Oxygen)	Relative Rates of Absorption
$LaNi_5$	−7,200	1.52	Small	Fast
$LaCuNi_4$	−7,500	1.35	Small	Fast
$La_{0.7}Ce_{0.3}Ni_5$	−7,000	1.6	Small	Fast
$SmCO_5$	−6,500	0.67	Small	Fast
$MmNi_5$	−6,500	1.5	Small	Fast
$Mm_{0.85}Ce_{0.15}Ni_5$	−6,500	1.5	Small	Fast
Vanadium	−9,600	5.9	Large	Fast
Niobium	−7,000	2.1	Large	
Magnesium	−17,800	7.6	Large	Slow
FeTi	−5,500	1.8	Large	Fast
$Mg_{0.93}Ni_{0.07}$	−17,000	5.7	Large	Fast
V(0.93%Si)	−9,600	5.6	Large	Fast

* Mm = "mischmetal," a mixture of rare earth metals in their naturally occurring composition.

Two design schemes have been developed by Brookhaven National Laboratory for an FeTi-hydride, hydrogen-storage system.[26] The major difference between the two designs is the method of system heat transfer for metal hydriding and dehydriding. One scheme (circulating hydrogen gas) uses gaseous hydrogen as the heat-transfer fluid for cooling the hydride bed during hydriding and for providing heat of dissociation during dehydriding. Development of this concept has ceased because a large quantity of hydrogen (50 times as much as is being stored) is required.

Table 11-7. HYDRIDE RESEARCH IN PROGRESS

Organization	Project
Brookhaven National Laboratory	Alloy hydrides — properties Iron-titanium — engineering design Peakshaving system design
Public Service Electric and Gas Co.	Peakshaving demonstration "Gas-electric transformer" system analysis
Billings Energy Research Corp.	Iron titanium for vehicles
Ames National Laboratory (Iowa)	Basic rare-earth hydride chemistry
Allied Chemical Corp.	Basic hydride chemistry — alloys
Phillips Research	Lanthanum-nickel — basic chemistry
Denver Research Institute	Basic
University of Virginia	Basic
Sandia Laboratories	Basic
Daimler-Benz Ag	FeTi for automobiles
Battelle-Geneva	Basic
Harwell, U.K.	NiH_2 battery

The other scheme uses water, circulated in tubes throughout a fixed hydride bed, for heat transfer. Hydrogen is only circulated in the metal-alloy-containment (FeTi) section. With this system, a greater overall heat-transfer coefficient is obtained. Also, attrition (metal-alloy breakdown into small particles) resulting from the passage of hydrogen through the bed throughout its lifetime is minimized. The rate of attrition would be more rapid in a circulating-gas design because a large quantity of hydrogen is circulated. A small fixed-bed hydride system was subjected to an endurance test of 1200 cycles. (Hydriding and dehydriding equals one cycle.) Test results indicate that because of the attrition of metal particles, the hydride-bed pressure drop increased from a few inches water column to about 15 psia.

Brookhaven is currently examining the effect of the impurities contained in the hydrogen on hydride-bed performance. Oxygen (from 15 to 20 ppm), carbon monoxide, hydrocarbons, and water are expected to reduce the hydrogen-storage capacity of the hydride bed.[28]

Capital cost estimates for a fixed-bed, hydride-storage system are not reliable because they are not associated with complete plant design. Researchers at Brookhaven[25] have made a preliminary current-capital-cost estimate of $5/kWhr for a hydride-storage system operating at 32 atm, assuming high-pressure hydrogen is available for hydriding. This figure can then be multiplied by a total hydride-bed charging time (e.g., 10 hours) to arrive at a hydride-system capital cost (here, $50/kW). Brookhaven[25] personnel also pointed out that the fixed-bed, hydride-storage system would be independent of "economies of scale" because the system would be modular in design. However, the optimum modular size has not yet been determined.

Brookhaven has built a fixed-bed, hydride-storage system for Public Service Electric and Gas Co.'s experimental energy-storage system.[29] This reservoir was designed for use with an electrolyzer and fuel cell. It will take up hydrogen at a rate greater than 1.5 lb/hr and will deliver it at a rate greater than 1.0 lb/hr. (Its working capacity is significantly more than the 10 pounds of hydrogen originally specified.) A compressor is required to pressurize the hydrogen leaving the electrolyzer so that a practical sorption rate is obtained. The temperature and flow rate of the water in the heat-exchanger tubes are also important factors in sorption and desorption rates. The last two factors will be capital-intensive factors in the design of larger hydride-storage systems.

The cycle efficiency of a metal-hydride-storage system could be greater than 90%. The efficiency of the system is defined as the lower heating value of the hydrogen put into storage minus the power consumed by the hydriding-dehydriding process divided by the lower heating value of the hydrogen put into storage.

Liquid-Hydrogen Storage

The most promising application for cryogenic hydrogen lies in bulk transportation of energy by rail or truck, with certain reservations. According to Linde,[16] hydrogen should be liquefied only when long-distance transmission is required and no pipelines are available.

At the hydrogen-usage location, storage capacity for greater than 1 million gallons could be required. Liquid hydrogen has been stored in a container of about this volume at NASA Kennedy Space Center. There are several smaller liquid-hydrogen storage tanks, sized from 200,000 to 300,000 gallons, at other NASA installations. Typically, liquid-hydrogen storage for private industry ranges from 15,000 to 26,000 gallons. Smaller liquid-hydrogen tanks (from 3000 to 6000 gallons) have also been installed for industrial use. Because of the extremely low temperature of liquid hydrogen (–423° F), double-walled, vacuum-insulated dewar storage vessels are required to minimize evaporation losses and to prevent condensation of air. The spherical vessel shape is a result of design constraints posed by the vacuum-jacketed insulation system. For some containers, daily boil-off losses are as low as about 0.5%. Materials compatible with liquid-hydrogen temperatures, such as stainless steel (300 series, typically) or aluminum alloys, must be used for the inner liner. Capital costs for vacuum-insulated, liquid-hydrogen storage tanks (of larger capacities) are between $2 and $4/gal of liquid hydrogen stored.

The liquid-hydrogen transfer and handling lines that were used successfully in the space program are very expensive. Cryogenic instrumentation has not advanced significantly in the last 10 years. Instruments suitable for aerospace applications are too costly for most commercial application, so rugged and reliable instruments that can be inexpensively mass-produced are needed.[14]

It might be possible to store large volumes of liquid hydrogen below ground. Some differences[10] between above- and belowground storage systems for LNG include –

1. Gradual freezing of the soil adjacent to underground storage areas, resulting in lower temperature gradients than with aboveground systems
2. Contribution by the frozen area of some additional thermal-insulating value beyond that of any applied insulation
3. Reduction of liquid-spill problems because of the frozen-earth wall surrounding the area
4. Requirement of more soil investigation and an increased site dependence with underground systems.

The fact that the temperature of liquid hydrogen is much lower than that of LNG will amplify these four observations. In order to reduce evaporation losses to the same level as for LNG, liquid-hydrogen storage will require more insulation of underground containers. In addition, a liner that is resistant to hydrogen-gas permeation will be required to prevent gas from leaking into the insulation. There should be no appreciable difference in the effect of the liquid hydrogen on the soil, except that greater areas around the storage site will be affected because of the greater temperature gradient.

The three forms of underground liquid-hydrogen storage that could be investigated to determine their technical and economic aspects are[10] —

1. Frozen, in-ground storage (excavated pit)
2. Prestressed-concrete-tank storage (underground)
3. Underground-cavern storage.

In addition to the cost of storage, handling, and transmission equipment for liquid hydrogen, the cost of liquefying the hydrogen must also be analyzed because it can far outweigh storage costs.[17] A hydrogen liquefier typically utilizes a nitrogen precooler-expander process in which hydrogen is recycled to provide refrigeration at three temperature levels below 80 ^{0}K. Two levels of refrigeration are provided by the hydrogen turbines, and the third is achieved by Joule-Thompson throttling of a portion of the high-pressure recycle hydrogen.[19]

In addition to the work required to cool and liquefy the hydrogen, there is another energy-consuming process encountered in liquefaction that results from differences in the electron spins of the hydrogen nuclei in the molecule. Hydrogen molecules that have symmetric nuclear spins are referred to as ortho hydrogen (oH_2), and those that have asymmetric spins are referred to as para hydrogen (pH_2). Hydrogen is a mixture of oH_2 and pH_2 at an equilibrium ratio, which is a function of temperature. The equilibrium para composition is about 25% at ambient room temperature and above. However, the para content increases with decreasing temperature, reaching an equilibrium composition of 99.79% pH_2 at the atmospheric boiling point of liquid hydrogen, 20.39 ^{0}K.[19]

Consideration must be given to the two hydrogen forms because of their difference in energy. At any temperature, the para form represents the lower energy state. To liquefy hydrogen and to maintain it in a stable state, sufficient energy must be removed not only to cool and liquefy the hydrogen, but also to convert the oH_2 to pH_2. In converting oH_2 to pH_2, 609 Btu/lb-mol (which exceeds the heat of vaporization of oH_2, 385 Btu/lb-mol) must be removed. The total enthalpy change in liquefying oH_2 and converting it to 99.79% pH_2 once it is cooled to liquefaction temperature is, therefore, 840 Btu/lb-mol.

At and above 80 ^{0}K, refrigeration is provided by 1) a stream of cold nitrogen gas that is used to help precool the combined feed and recycle stream and 2) a stream of nitrogen liquid that is used for additional cooling. The hydrogen feed stream is cooled, continuously, down to the temperature of the exhaust from the cold turbine, after which it is throttled, passed through a catalytic converter for trimming purposes, and then subcooled in heat exchange with hydrogen boiling at low pressure.[19]

Cold exhaust streams from the expanders are warmed in counter-current heat exchange with cooling hydrogen streams, are combined, and are finally returned to the suction of the recycle compressor. Vaporized hydrogen from the final subcooler is combined with flash vapor from throttling and is then warmed in heat exchange with a cooling stream and returned to the suction of the subcooling-fluid compressor, which in turn discharges to the suction of the recycle compressor.[19]

Linde considers the estimated capital-equipment cost for a liquid-hydrogen plant with capacity greater than 10 tons/day (and throughout the medium plant size range) to be approximately $500,000/ton of hydrogen liquefied per day.[16] Much higher relative capital-equipment costs per output would be associated with small plant sizes, and very large plants would have lower relative capital costs per output than medium-size plants. Air Products and Chemicals, Inc., considers hydrogen-liquefaction-plant design economically undesirable below a 15 ton/day plant size because the high cost of component parts are reflected in high hydrogen-product costs.[7]

The reversible work necessary to liquefy hydrogen has been determined to be 1.773 kWhr/lb in going from 308 °K (95 °F) at 1 atm to the final condition of liquid hydrogen (97% para content) at 20.57°K and 135 psia. Under these conditions, the minimum energy requirement, using current technology, is 4.9 kWhr/lb. More than half of the energy losses can be attributed to the compressor. This figure indicates that approximately one-third the lower combustion value of a pound of hydrogen is needed to liquefy it, not including energy that might be needed to purify the gaseous hydrogen feed to cryogenic standards. The practical cycle efficiency of a hydrogen-liquefaction storage cycle, defined as the net heating value of the hydrogen minus the power consumed divided by the net heating value of the hydrogen, would be from 65% to 68%.

Conversion from ortho to para hydrogen proceeds spontaneously, but at a slow rate. Autoconversion of liquid hydrogen in storage will occur, resulting in a severe boil-off (about 1%/hr, neglecting heat effects) that will decrease with increasing conversion.

As the para content of the liquefied hydrogen approaches equilibrium, the power requirement for liquefaction increases, but the storage loss decreases. Consequently, the optimum para content of the product is a function of the mean storage time. For example, calculations[19] show that for 95% para liquid hydrogen, the conversion boil-off loss is 1.24% over a 2-week period. If the plant were to produce only 75% para, product boil-off losses over a 2-week period would be 19.1%.[19] However, for each initial composition, a break-even period exists during which the energy cost for conversion equals the energy cost for the vaporized hydrogen. If the hydrogen is used within the break-even time limit, partial conversion is advantageous with respect to energy consumption.

Underground Compressed-Gas Storage

The natural gas industry currently relies on cheap underground gas storage to meet seasonal peak gas demands. There are five underground-gas-storage systems that may be applicable to hydrogen-gas storage[22]:

1. Depleted oil and gas fields
2. Aquifers (subterranean porous rock structures containing water)
3. Salt cavities

4. Natural or mined cavities in rock

5. Cavities induced by nuclear explosions.

A description of the above methods and comments on their applicability for hydrogen-gas storage are provided. A natural gas analogy is given in some instances.

Depleted Oil and Gas Reservoirs

Natural gas has been successfully stored in depleted gas and oil reservoirs. The gas is stored in the void spaces of porous rock structures such as sandstone. Sufficient porosity (providing storage volume) and permeability (to permit movement of gas into and out of the structure) are essential features. A leak-tight "cap rock" formation on top of the storage structure provides a seal. Cushion or nonrecoverable gas is required, and the pressure-injection level will determine the final quantity of gas stored.

This method may be considered for hydrogen storage because the gas-tightness of the reservoir does not depend on the nature of the gas contained. Cap rock is usually saturated with water. Capillary resistance of water within the pores will form a positive seal, regardless of gas-molecule size. Thus, hydrogen should be storable at pressures equivalent to those employed with natural gas.

For several years, the U.S. Department of the Interior, Division of Helium, has injected helium (a "leaky" gas) at a pressure of 817 psi into the Cliffside Field in Amarillo, Texas. Careful retention monitoring of the field should provide valuable information concerning possible hydrogen storage.

Aquifer Storage

Bearing much resemblance to depleted-gas-field storage, but having no native hydrocarbon deposits, aquifer storage of gas is also used. Injected gas displaces water in porous rock, forming a trapped "bubble" at or near local hydrostatic pressure. The gas-water interface is highly mobile, a function of the injection-withdrawal cycle. Gas storage is intact as long as "threshold pressure" (a gas pressure high enough to completely displace the water from the cap rock pores) is not exceeded and the aquifer maximum-volume limit is heeded.

Aquifer storage of hydrogen seems to be quite possible because the water-saturated cap rock seal can be used. An aquifer storage field in Beynes, near Paris, was operated successfully on manufactured gas (about one-half hydrogen) for about 10 years.

Salt-Cavern Storage

Salt caverns, formed in underground salt strata and salt domes by "solution mining," have been used for the storage of LPG and for limited storage of natural gas. The technique for forming salt cavities via solution mining is well developed. Basically, water is pumped in, and brine is removed so the cavity geometry is leached out. Hydrogen storage in salt cavities has already been demonstrated by the British Chemical Industry.[31] Salt strata occur in various parts of the United States, and the estimated total U.S. capacity of salt-cavity storage wells is currently about 200 million barrels. However, additional capacity can be readily added.

Natural or Mined Cavities

Where appropriate porous rock structures, salt strata, or salt domes do not exist, it is possible that natural or mined cavities could be used for the storage of gases (including hydrogen). However, experience in this area is limited. Assuming that a sealing structure functionally analogous to water-saturated cap rock exists, such cavities should be reasonably leak-tight.

Cavities Induced by Nuclear Explosions

The energy released by a subterranean nuclear explosion causes an adiabatic shock wave with temperatures and pressures on the order of 1 million ^{0}F and 1 million atm, respectively. A nearly spherical shape remains after condensation and solidification of the molten phase. However, if the reflected shock wave returns from the surface with too much force, the cavity will collapse, resulting in a "chimney formation." Much remains to be learned about threshold pressure, impermeability, fracture susceptibility, and radiation decay before gas can be stored in such cavities.

An example of such a structure is the stable spherical cavity with a radius of 87 feet at a depth of 1200 feet produced by the "Gnome Event."[32] If gas pressures of up to 1 psi/ft could be maintained, approximately 290 million SCF of natural gas could be stored there.

Linepack Compressed-Gas Storage

If pipelines of conventional sizes and numbers, comparable to those used in natural gas systems, are incorporated in the hydrogen-transmission system, linepack storage will probably play only a small role because of hydrogen's lower volumetric heating value (compared with that of natural gas). However, if pipes of larger diameters are incorporated in the systems, linepack storage could become significant.

Underwater Compressed-Gas Storage

Underwater gas storage at the equivalent hydrostatic pressure in low-cost, thin-walled containment membranes shows great promise.[32] A spherical container can be used as a storage vessel. At greater depths, the water pressure and constant low temperatures are advantageous for the storage of large quantities of gas. Another advantage would be afforded by underwater storage in oceans, in which case the salt in the water would prevent hydrate formation. Safety, leakage, collection, and contamination problems will be held to a minimum in underwater hydrogen storage.

Aboveground Compressed-Gas Storage

Current technology allows for the aboveground storage of hydrogen in medium- and high-pressure vessels. Much operating experience has been obtained in the pressure-vessel storage of hydrogen. Most pressure-vessel materials are not susceptible to hydrogen embrittlement. High-pressure storage is technically sound; however, high capital costs are involved. Pressure vessels are currently available from United States Steel Corp. for large-scale storage of hydrogen at 500, 1295, and 2400 psi, as shown in Table 11-8.

Concluding Comments

Three systems of aboveground storage may be considered for hydrogen-energy storage. Both hydrogen liquefaction with subsequent storage and compression of hydrogen with high-pressure tube storage are currently in use. Metal-hydride storage is currently under development.

Table 11-8. PROPERTIES OF U.S. STEEL CORP.'S HYDROGEN-STORAGE VESSELS

Pressure, psi	Size	No. of Vessels Required to Store 10^6 SCF	Vessel Cost, $	Vessel Mounting Cost, $	Vessel Manifolding Cost, $	Total Capital Cost for 10^6 SCF Capacity, $\$10^6$
500	24-in. OD 40 ft long	265	3300	540	250	1.08
1295	24-in. OD 40 ft long	116	3500	540	275	0.50
2450	24-in. OD 20.5 ft long	136	3900	540	300	0.65

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Selection of a hydrogen-storage scheme will depend on many application features, including storage capacity, duration of storage, hydrogen-charging capacity, amount of storage-system use, and associated costs. Table 11-9 is a comparison of some of the characteristics of the three methods proposed for aboveground hydrogen storage.

Table 11-9. RELATIVE COMPARISON OF HYDROGEN-STORAGE METHODS

Point of Comparison	Metal Hydride	Liquid	Compressed Gas
Capital Equipment Cost, $/1000 SCF	400-600	1000-1300	800-1100
Energy Expenditure, kWhr/lb of hydrogen storage cycle	0.8-1	4-5	0.5-1
Intermittent-Operation Capability	Good	Fair	Good
Hydrogen Volume per Container Volume	Medium	High	Low
Storage Stability With Full Storage Volume	Good	Medium	Medium
Storage-Vessel Cost as % of Total Storage Cost	Medium	Low	High
Equipment Necessary to Admit Hydrogen Into Storage as % of Total Storage Cost	Medium	High	Low

Several alternative systems for the underground storage of gaseous hydrogen exist, and abundant experience with underground storage of natural gas has been obtained in connection with depleted gas fields and aquifer reservoirs. An advantage with these methods of hydrogen storage is the water-sealing property of cap rock, which prevents diffusion of hydrogen gas.

Much less experience has been gained with salt cavities and natural and mined cavities. Many technical and economical advantages are claimed for the underground storage of hydrogen gas. Further investigation of each underground method of gas storage is warranted.

Hydrogen in Gas-Distribution Systems

Introduction

Although there are many research and development programs (recent and current) related to hydrogen energy, none deals directly with testing the conventional gas-distribution system for use with hydrogen. Additionally, there have been no demonstrations of hydrogen delivery by conventional (modern) gas-distribution systems. Hence, very little information is available on the compatibility of this system with hydrogen. We can only describe the natural-gas-distribution system in the United States and note the compatibilities and problems expected in use with hydrogen.

The Gas-Distribution System

The U.S. gas-distribution system typically consists of one or more networks of piping that carry the gas to the consumers from the various sources of supply: city-gate station, gas-storage facilities, and gas-manufacturing plants. Figure 11-5 is a schematic of the various components of a representative distribution system that includes a manufactured gas supply.[6] The latest available statistics show the purchased and produced gas to be 18,730 trillion Btu of natural gases per year and 30 trillion Btu of manufactured and substitute natural gas per year. (Annual production of SNG is growing at a very rapid rate.[2]) Hence, the primary source of gas for most distribution systems is pipeline natural gas fed through one or more city-gate stations. The basic functions of these stations are to meter the gas and to reduce the pressure of the gas from that of the pipeline to that of the distribution system. Most stations measure the gas with orifice meters. Controlled pressure reduction is accomplished with pressure regulators that control the rate of

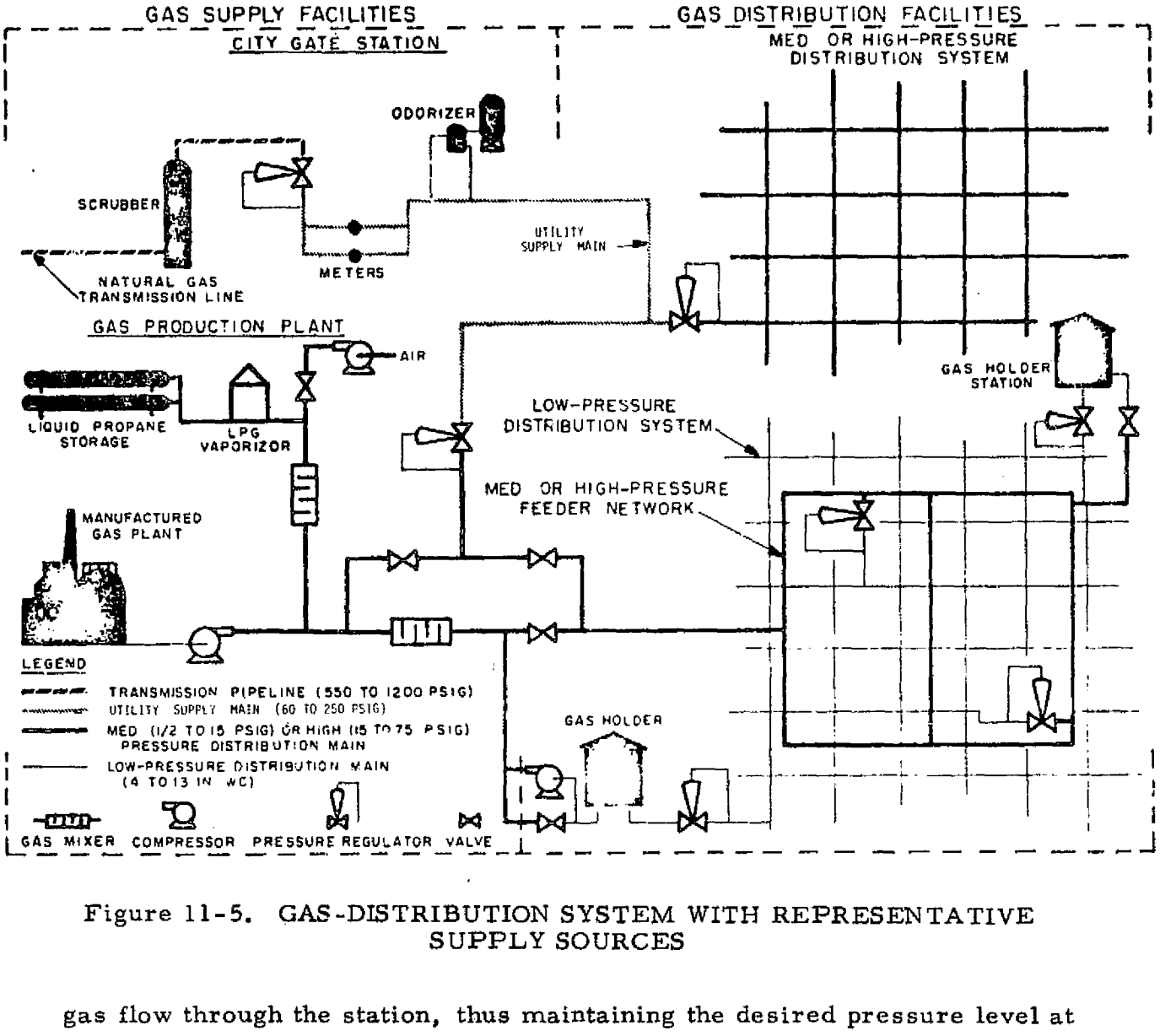

Figure 11-5. GAS-DISTRIBUTION SYSTEM WITH REPRESENTATIVE SUPPLY SOURCES

gas flow through the station, thus maintaining the desired pressure level at its outlet.

Before the gas leaves a city-gate station, a small, controlled amount of a substance with a strong, penetrating odor is injected into it with an odorizer. This odorant warns customers of the presence of unburned gas before it can accumulate to a hazardous concentration. The piping that transmits the gas from the city-gate station to the remainder of the distribution system is the supply main. Beyond the supply main, the piping in the distribution system can be categorized as [6]—

1. Trunk mains, transmitting gas from a major source (such as a supply main) to feeder mains

2. Feeder mains, transmitting gas from trunk mains to distributor mains, as well as to the services connected to them

3. Distributor mains, supplying gas primarily to services

4. Services, delivering gas from a main to customers' gas meters.

Many distribution systems consist of several superimposed networks of piping operating at different pressures. Gas from high-pressure supply mains may be fed through pressure regulators into high-, medium-, or low-pressure distribution networks. High-pressure distribution networks, operated at from 15 to 75 psig, are of two types:

1. Networks that serve customers directly

2. Networks that are used primarily to feed gas into medium- (from 1/2 to 15 psi) or low-pressure (4 to 12-inch water column) distribution networks.

Although classification of piping networks by pressure level is quite common, there is no standard terminology or pressure range covered by each classification.

The fuel lines of residential customers are usually operated at pressures of from 4 to 10-inch water column, the pressure required for proper appliance performance. Consequently, it is necessary to install a service regulator in each residence fed directly by a medium- or high-pressure distribution system. This regulator reduces the pressure from that of the main to that of the fuel line.

The basic distribution system in most older, large cities is a low-pressure, cast-iron pipe system. Most of the piping in these systems was laid during the manufactured-gas era when gas (containing up to 50% hydrogen) was produced at low pressure and compression was a relatively expensive operation. With higher pressure natural gas now available, major portions of new distribution systems are medium- or high-pressure networks of steel. Consequently, most older low-pressure systems are now ringed and overlaid with medium- and high-pressure piping grids.[6] Although these modern distribution grids were designed for use with natural gas and have never been tested with hydrogen, major problems in use with hydrogen are not anticipated. A

principal concern, however, is the greater tendency of hydrogen to leak from a pressurized system.

A tremendous variety of pipes and fittings have been used, but one trend predominates in newly installed gas-distribution systems — the increased use of plastic pipes and fittings for mains of 2-inch diameter and smaller (medium- and low-pressure networks) and for services. According to a recent survey, about 87% of the gas utility companies are now installing plastic pipes for new and replacement mains, and about 92% use plastic for new and replacement services.[9] On a length or footage basis, over 55% of the distribution piping to be installed during 1975 will be plastic. At present, however, the composition of the total in-place mains and services is approximately as shown in Table 11-10.

Table 11-10. DISTRIBUTION-SYSTEM PIPE MATERIALS

Pipe Material	Mains, % of total (footage basis)	Service, % of total (number basis)
Steel	81	83
Cast and Ductile Iron	12	2
Copper	1	6
Plastic	7	9

In addition to the pipes and fittings, there are numerous flow-metering and -control devices such as valves, pressure regulators, and meters. Following is a partial list of the common materials of construction for components in distribution systems and some of their predominant uses:

- Gray cast iron (old mains)
- Ductile and wrought iron (mains)
- Copper (services and main inserts)
- Steel (mains and services)
- Brass (valves)
- Polyethylene (services and mains)
- Polyvinylchloride (services and mains)
- Fiberglass-reinforced epoxy (services and mains)

- Natural and synthetic rubber and elastomers (mechanical joint seals and meter diaphragms)
- Lead and jute (sealer for bell and spigot joints)
- Cast aluminum (meter housings and regulator parts)
- Cadmium-plated steel (internal regulator parts)
- Cork and gasket materials (meter and instrument gaskets)
- Miscellaneous plastics — ABS, CAB, PB, nylon, etc. (services and internal instrument parts).

From the diversity of equipment, operating conditions, and materials of construction, it is evident that compatibility of the distribution system with hydrogen requires verification by demonstration. Any statement that hydrogen or hydrogen-rich gases can be adequately and safely delivered to the customer through the in-place natural-gas-distribution system is a presumption.

Hydrogen Compatibility and Problem Areas

Volumetric Flow

Because of the vast differences among U.S. distribution networks (in terms of types of equipment, materials of construction, operation conditions, and age), it would be meaningless at this stage to assess overall compatibility for a single "typical" system or to attempt to quantitatively describe a "typical" system's conditions of operation with hydrogen. Generally, the conditions of operation will be determined by delivery of the quantity of hydrogen equivalent in high heating value to that of natural gas delivery. This will necessitate a proportionate increase in the volumetric flow of hydrogen relative to natural gas. This means that the volumetric flow meter used for measuring gas delivery could be undersized (by a factor of as much as 3) for hydrogen usage.

Except in some small-diameter (service) lines, the flow in natural-gas-distribution systems is (partially) turbulent. The Reynolds number, which mathematically characterizes the flow, is directly dependent upon pipe diameter and gas velocity and density and is inversely dependent upon gas viscosity. If we consider hydrogen for energy delivery equivalent to that of natural gas in a given pipe, we might have a tripled gas velocity, a 20% decrease in viscosity, and an 87% decrease in density (compared with methane). As a result, the Reynolds number for hydrogen flow could be less than half that for natural gas flow. If the Reynolds number falls to below about 2000, the resulting laminar flow

with viscous drag could require significantly higher operating pressures and pressure drops for adequate flow and energy delivery.

Odorants and Illuminants

Apparently the sulfur compounds now used to odorize natural gas are compatible with hydrogen and would, therefore, be satisfactory hydrogen odorants. Because odorants have to be added on a volume basis and because the volume of hydrogen used will be 3 times that of natural gas (on an equivalent energy basis), 3 times the quantity of odorant will be required, thus maintaining the same percentages. The odorant would be burned at the appliance. Odorization should present no pollution problem, and the added cost would be insignificant.

The addition of an illuminant, which would make the hydrogen flame visible, simultaneously with an odorant should be considered. This would facilitate hydrogen use in open-flame appliances and assist in the adjustment of burners and pilots. No suitable illuminant has yet been identified, but two types of materials would be appropriate. One is a small amount of an aromatic-type organic material that would burn with a yellow flame. The other is a trace of a volatile organo-metallic sodium compound that would give the flame the characteristic sodium-yellow color. Experimentation is required to determine whether or not either of these approaches would be useful and to determine the optimum quantities to be added.

The addition of any foreign material, especially sulfur-bearing odorants, to hydrogen used in catalytic processes could cause considerable problems. Representatives of Air Products and Chemicals, Inc., told us that they had considered odorizing the hydrogen in the company's Houston transmission line, but several of the industrial users on the line could not tolerate the presence of even traces of sulfur compounds. Similar considerations may apply to the use of hydrogen in catalytic burners. It is technically possible to remove the odorant immediately before the catalytic bed, but in some applications this would be inconvenient and would add to the cost. An alternative worthy of consideration for future experimental work is to develop an odorizing material that does not contain sulfur and that does not interfere with catalysts. It may be appropriate to introduce such a "new smell" with the introduction of the "new gas" to the public, in which case a suitable odorant must be ready for application as soon as the first general use of hydrogen is introduced.

Leakage

The rate of the loss of hydrogen through leaks, whether fractures, corrosion pinholes, or leaky seals, is about 3 times greater (on a volume basis) than that of natural gas. The rate of energy loss through the leak is about the same as for natural gas; but in a confined space, the lower flammable limit of hydrogen (4.0%) will be reached in a quarter of the time required for natural gas to reach its limit.[8] Hydrogen's rapid diffusivity, 2.8 times faster than that of natural gas, will allow it to permeate rapidly through dry soil and crushed rock and therefore to escape from the point of leakage. Once it reaches the air, its low density will cause it to rise rapidly.

Cast-iron and steel pipes are, for all usual purposes, almost impermeable to both hydrogen and natural gas at ambient temperatures. In fact, even though the permeability rate of hydrogen is higher than that of natural gas, it is still so small that it is insignificant. This should also be the case for sealing materials; but to be sure, experimental confirmation should be obtained for typical seals.

Hydrogen's permeation of plastic pipes, however, warrants further consideration. Some permeability measurements of typical plastic piping compounds have been made. In these studies, the ratio of hydrogen to natural gas permeation varies widely – between about 7:1 for polyethylene and 88:1 for ABS. Table 11-11 shows some relative permeation data obtained by Battelle Memorial Institute.[1]

Table 11-11. GAS PERMEATION OF PLASTIC PIPING COMPOUNDS

Material	Methane Permeation — 10^{-3} CF/sq ft-atm-day —	Hydrogen Permeation	Relative Permeation (Hydrogen/Methane)
Acrylonitrite-Butadiene Styrene, ABS-1-2	0.59	51.71	87.6
Cellulose Acetate-Butyrate, CAB/MH	11.8	157.0	13.3
Polypropylene	1.6	20.2	12.6
Polyethylene PE III-3	2.3	15.7	6.8
Polyvinyl Chloride, PVC-II-I	0.2	13.7	68.5

In the case of PVC pipe, the loss of hydrogen will be from 6 to 8 times the loss of natural gas (on a volume basis), but in absolute terms this amounts to only 83.8 SCF/yr per mile of 4-inch pipe (with a wall thickness of 0.33 inch) operated at 1 atm (or 15 psig). In comparison, Heath Survey Consultants[24] reports that a typical leakage rate for existing gas systems is between 100,000 and 4 million SCF/yr per mile of 3-inch "equivalent" pipe. Figures obtained from England indicate that a typical rate of leakage from cast-iron mains that carry manufactured gas (50% hydrogen) at a pressure of 6-inch water column is 20 SCF/hr per 1000 yards of main, or approximately 800,000 SCF/yr-mile. This apparently tolerated leakage rate makes the diffusion rate of hydrogen through PVC pipes appear insignificant.

Losses of hydrogen by diffusion through other plastic materials are higher than through PVC. Losses through CAB and ABS will be 11 and 4 times as great, respectively. In the latter case, the loss will be more than 3000 SCF/yr per mile of 4-inch pipe. Before we conclude that these leakage rates are not hazardous, experimental measurements should be made of the rate of diffusion of hydrogen through a backfilled trench and under pavement or frozen ground. It appears that PVC and polyethylene are preferable to ABS and CAB. However, long-range testing of actual pipe sections under service conditions to obtain practical proof of their suitability would be worthwhile.

Most of the serious gas leaks in distribution systems are caused by damage done to mains by construction contractors. With plastic pipe, severing of the line is common, whereas steel pipes usually only bend or crack. Fire rearely results from such an accident. With hydrogen, however, a fire will almost certainly occur if an ignition source is present. Static charges frequently build up on the inside of plastic pipes, and the fracture of a metal pipe could be accompanied by friction sparks — either of which could cause ignition. Thus, we might expect a higher incidence of fire cause by accidental damage to hydrogen pipes. This may be considered fortunate because a buildup of explosive mixtures, as can happen with unignited leaks, is prevented. However, different operational practices may have to be devised to cope with this aspect.

C.4

Leaks in industrial hydrogen systems are detected by combustible-gas detectors. A hazard unique to hydrogen leaks in aboveground hydrogen pipework is that occasionally the leaking gas ignites because of a spark from static friction caused by the leak. The resulting "invisible" flame cannot be seen in daylight. Because of this problem, flame detectors[24] have been developed for hydrogen systems.

Line Purging and Maintenance

An area of serious concern is the purging requirements for pipes, both when bringing new mains into service and when repairing existing mains. Use of an inert gas to sweep out the air or to sweep out the gas already in a used main may be necessary because the wide flammability limits of hydrogen (from 4% to 75% compared with from 5% to 15% for natural gas) would more frequently result in hazardous conditions in the main. With natural gas, welding operations can be performed when the gas-air mixture in the line is more than 15% gas. With hydrogen, however, one would have to ensure that the hydrogen air mixture was safely above 75% hydrogen. Use of some form of an oxygen-level indicator may be necessary to ensure that the line has been adequately purged. Purging procedures will have to be established through experimentation.

Peculiar Temperature Effects

Unlike methane or natural gas, hydrogen has a maximum Joule-Thompson inversion temperature of $-109^{0}F$, far below ambient temperatures. Therefore, at ambient temperatures hydrogen undergoes a temperature increase upon throttled expansion. The extent of the temperature increase depends upon the pressure drop, the initial gas temperature, and the rate of heat exchange between the hydrogen and the environment. This Joule-Thompson effect could be significant at leaks because it would increase the chances of ignition, and it could be significant with plastic components. Thermoplastic pipe for natural gas service, for instance, is not required to be pressure tested (at 50 psig or 150% of operating pressure, whichever is greater) at temperatures above $100^{0}F$.[21]

Concluding Comments

It is possible that certain localized areas may be selected for complete transition from natural gas to hydrogen service to accelerate the use of nonfossil energy sources or to provide a market for a storable, synthetic chemical fuel. Another possibility, in a shorter time frame, is that of supplying hydrogen produced from coal, oil shale, or nuclear sources (off-peak power) to certain specialized industrial users for use as a fuel or as a chemical feedstock (for example, to ammonia producers) to relieve the shortage of natural gas. In any of these circumstances, it will be necessary to demonstrate and verify that gas-distribution equipment is compatible with hydrogen and that conventional or suitably modified techniques for handling natural gas are acceptable for use with hydrogen.

References Cited in This Section

1. American Gas Association, The Development of Improved Plastic Pipe for Gas Distribution Purposes. Arlington, Va., 1968.

2. American Gas Association, 1973 Gas Facts. Arlington, Va., 1973.

3. Beghi, G. et al., Hydrogen, Oxygen, and Natural Gas by Pipeline: Comparative Transport Costs. Ispra (Varese), Italy: EURATOM, n.d.

4. Falcone, C. A., "Hydrogen Transmission: the Significance of Efficiency." Paper No. C 75 111-0 presented at the IEEE PES Winter Meeting, New York, January 26-31, 1975.

5. Fletcher, E. E. and Elsea, A. R., "Evaluation of the Influences of Absorbed and Adsorbed Hydrogen on the Mechanical Properties and Fracture Behavior of Materials to be Used in a Hydrogen-Gas Transmission System," Summary Report to IGT by Battelle Lab., Columbus, February 1974.

6. Forwalter, J., Ed., IGT Home Study Course — Gas Distribution. Chicago: Institute of Gas Technology, 1963.

7. Foust, P., Air Products and Chemicals, Inc., letter of March 25, 1975.

8. Gregory, D. P., "A Hydrogen-Energy System," Am. Gas Assoc. Cat. No. L21173. Arlington, Va.: American Gas Association, 1972.

9. Hale, D., Ed., "P&GJ Staff Report," Pipeline Gas J. 201, No. 13, 26 (1974) November.

10. Hallet, N. C., "Study, Cost, and System Analysis of Liquid Hydrogen Production," Air Products and Chemicals, Inc., Contract No. NASZ-3894, (1968) June.

11. Hampson, P. J. et al., "Will Hydrogen Transmission Replace Electricity?" Paper presented at Hydrogen Energy Fundamentals – a Symposium-Course, Miami Beach, March 3-5, 1975.

12. Hollenberg, J. G., "Hydrogen Pipeline Transmission." Paper presented at Hydrogen Energy Fundamentals – a Symposium-Course, Miami Beach, March 3-5, 1975.

13. Hord, J. et al., "Selected Topics on Hydrogen Fuel," Cryogenics Division National Bureau of Standards Paper No. NBSIR 75-803, (1975) January.

14. Hord, J., "Research Opportunities in Cryogenic Hydrogen-Energy System." Paper presented at Hydrogen Energy Fundamentals – a Symposium-Course. Miami Beach, March 3-5, 1975.

15. Icerman, L., "Relative Costs of Energy Transmission for Hydrogen, Natural Gas, and Electricity," Energy Sources 1, No. 4, 435-36.

16. Johnson, J., Union Carbide Linde Division, letter of March 24, 1975.

17. Johnson, J. E., "The Storage and Transporation of Synthetic Fuels," Oak Ridge National Laboratory Paper No. ORNL-TM-4307, September 1972.

18. Konopka, A. J. and Wurm, J., "Transmission of Gaseous Hydrogen." Paper presented at the Ninth IECEC, San Francisco, August 26-30, 1974.

19. Langley Research Center, "Survey Study of the Efficiency and Economics of Hydrogen Liquefaction," Contract NAS 1-13395. Hampton, Va., 1974.

20. Leeth, G. G., "Nuclear Heat Transmission Considerations." Paper presented at the First National Topical Meeting on Nuclear Process Heat Applications, Los Alamos, New Mexico, October 1-3, 1974.

21. "Minimum Federal Safety Standards for Gas Lines," Subpart J, Requirement 192.511 of the Code of Federal Regulations in Pipeline Gas J. 202, No. 4, 49 (1975) March 15.

22. Mitchell, G. M. and Smith, J. A., "Peak Shaving by Gas Storage," in Forwalter, J., Ed., IGT Home Study Course – Gas Distribution, 276. Chicago: Institute of Gas Technology, 1963.

23. Reynolds, R. A. and Slager, W. L., "Pipeline Transportation of Hydrogen." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami, March 1974.

24. Rosen, B., Dagan, V. H., and Proffit, R. C., Hydrogen Leak and Fire Protection, a Summary, Contract NAS 8-5604. Washington, D.C.: NASA, Technology Utilization Division, Office of Technology Utilization, 1970.

25. Salzano, F. J., Brookhaven National Laboratory, letter of March 1975.

26. Salzano, F. J., Ed., "Hydrogen Storage and Production in Utilities." First Annu. Rep. Brookhaven Natl. Lab. Upton, N.Y., July 1974.

27. Sharer, J. C. and Pangborn, J. P., "Utilization of Hydrogen As an Appliance Fuel," Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami, March 1974.

28. Strickland, G. G., Brookhaven National Laboratory, letter of March 1975.

29. Strickland, G. G. and Reilly, J. J., "Operating Manual for the PSE G Hydrogen Reservoir Containing Iron Titanium Hydride." Brookhaven National Laboratory Paper No. BNL50421, (1974) February.

30. Swisher, J. H. et al., "Survey of Hydrogen Compatibility Problems in Energy Storage and Energy Transmission Applications," Sandia Laboratories Rep. No. SAN074-8219, (1974) September.

31. Tatchell, J. A., "Hydrogen in the Chemical Industry." Lecture 4 at the Symposium on Prospects for the Hydrogen Economy, Queen Mary College, London, June 6, 1974.

32. Tek, M. R. and Wilkes, J. O., "New Concepts in Underground Storage of Natural Gas," University of Michigan Monograph prepared for the Pipeline Research Committee, Am. Gas Assoc. Cat. No. L00400, March 1966.

33. Wiswall, R. H. and Reilly, J. J., "Metal Hydrides for Energy," in Proc. Seventh Intersoc. Energy Convers. Eng. Conf., 1342 (1972) September.

12. INDUSTRIAL HYDROGEN UTILIZATION — W.J.D. Escher and D. P. Gregory

Present Industrial Uses of Hydrogen — an Overview

Hydrogen is one of the world's leading chemical intermediates. It is produced by a wide variety of processes and has a large number of applications. A concise and somewhat generalized illustration of the current major uses of hydrogen has been put forth by Air Products and Chemicals, Inc., and is presented here as Figure 12-1. In this "hydrogen tree," the major applications of hydrogen are shown as the lower branches, while the lesser uses are nearer the top.

The larger uses of hydrogen include ammonia production (56% of the 1970 world hydrogen market[3]), hydrotreatments of petroleum feedstocks (30%), and hydrogenations of petrochemicals and methanol synthesis (totaling 14%). Usually these applications require such large quantities of hydrogen that the hydrogen is produced onsite in an adjacent plant. In many cases, plants for these processes are sited close to a petroleum refinery or a chemical-works complex in which hydrogen is interchanged between processes, almost like a utility service. This hydrogen is commonly termed "captive hydrogen" because it is rarely included in intercompany sales or transmitted over more than a few thousand feet. In some cases, hydrogen mixed with other gases can be tolerated or may be needed for the application; thus the captive hydrogen may only consist of a low-purity hydrogen stream. It is difficult to obtain figures as to the scale of the captive-hydrogen market or the typical prices paid for the commodity.

The intermediate-sized applications of hydrogen, including basic industrial processes (especially soap and fat production), oxo-alcohol production, and the glass and metallurgical industries, are usually provided with relatively pure hydrogen delivered from a remote plant. Frequently, the source of hydrogen is interconnected with a refinery or chemical works. Hydrogen is supplied to the users either in the liquid (cryogenic) state by rail or tank truck or by a small, privately owned pipeline. This hydrogen is commonly termed "merchant hydrogen" and is handled by the industrial-gases industry. Because this hydrogen is usually marketed between companies

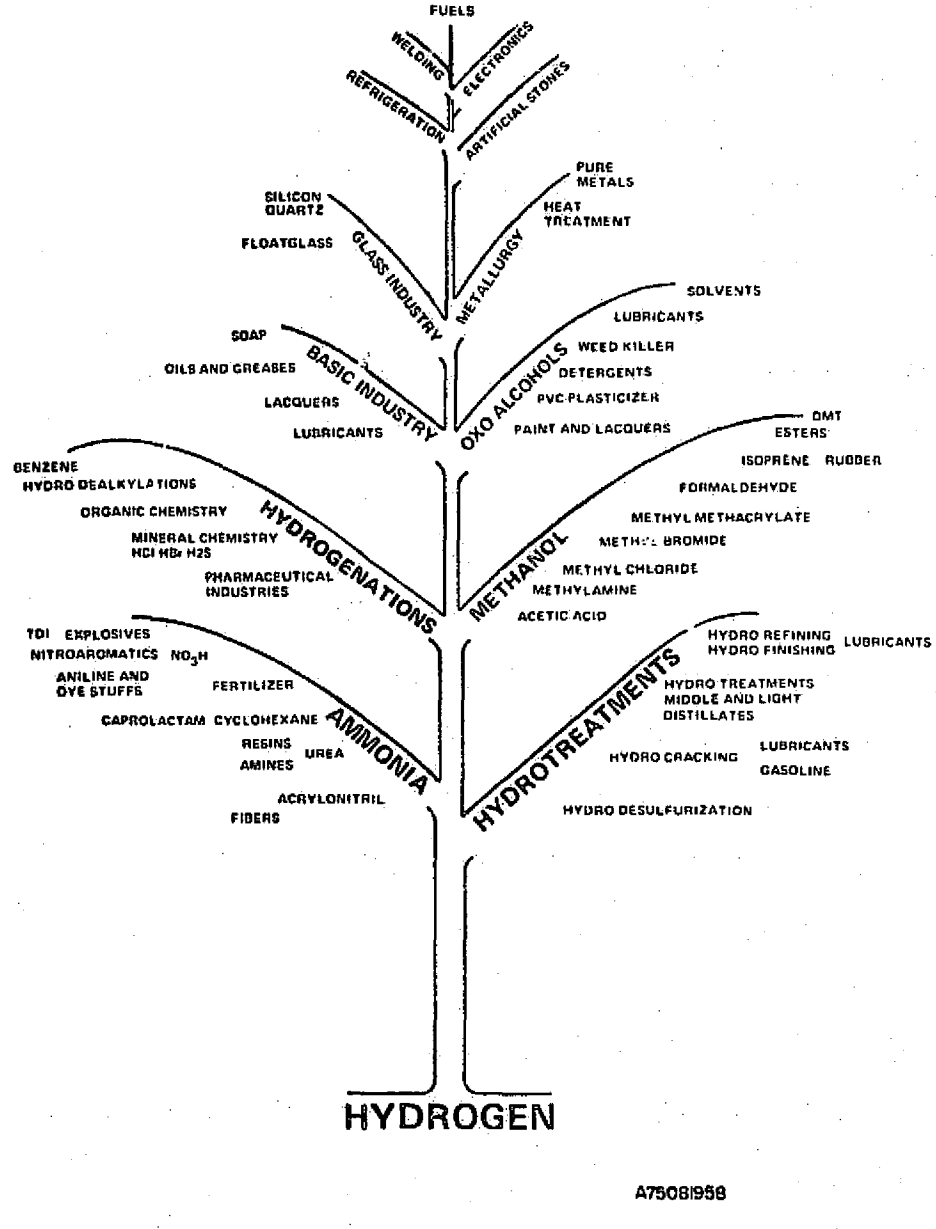

Figure 12-1. PRESENT MAJOR USES OF HYDROGEN
(Source: Air Products and Chemicals, Inc.)

and because it is usually handled in a relatively pure state, it is easier to find quantitative data for annual utilization rates and for typical prices for this hydrogen.

The smaller users of hydrogen typically take delivery of the hydrogen as gas in high-pressure cylinders or as the cryogenic liquid. An exception is the fuels application of hydrogen, which is a special case deserving independent discussion. There are many exceptions to the "typical" examples described here. Many of the smaller and intermediate users of hydrogen generate their own supplies from hydrocarbon feedstocks (usually natural gas), by cracking ammonia, or by the electrolysis of water.

The fuels applications of hydrogen are very small and are only justified in special cases, usually where by-product hydrogen streams are available and no more advantageous use can be made of them. Almost exclusively, fuels uses of hydrogen are tied to a captive-hydrogen type of operation, and delivery is usually by short pipelines. It is not usually economical to use hydrogen that has been purified and delivered as a liquid or as a high-pressure gas for a fuel gas.

According to the U.S. Department of Commerce, the U.S. merchant hydrogen market in 1974 was 72 billion SCF/yr. The growth rate from 1973 to 1974 was 11%. This growth rate is among the highest reported for high-volume inorganic and organic chemicals.

Projections for Hydrogen Utilization

The major markets for captive hydrogen are growing at rates that reflect the general trend of increased use of processed fuels, fertilizers, and high-volume chemicals. Major changes in this steady growth pattern cannot be predicted and are not anticipated. These markets do not represent major new uses for hydrogen, but the source of the hydrogen that they use is likely to undergo major changes in the foreseeable future. Most of the hydrogen used in these applications is produced from petroleum (in the refineries) or by steam reforming natural gas. It is important to consider the prospect for replacing these raw materials with more abundant ones, primarily coal or nonfossil sources. In general, the quality of the hydrogen or a hydrogen mixture made

from coal will be similar to that of the hydrogen made from other fossil fuels; however, hydrogen from nonfossil sources is likely to be relatively pure, and in order to utilize it, the user's process may have to be modified.

The uses of merchant hydrogen are also exhibiting growth rates tied to the economies of their individual industrial sectors, and no major new applications for this hydrogen are expected. The feedstocks used by the industrial-gas suppliers, particularly natural gas, are in extremely short supply. Therefore, serious and urgent consideration is being given to the use of coal, or perhaps nonfossil sources, for central-plant hydrogen production. Major changes by the gas suppliers are not likely to have any major effects on the hydrogen-use patterns.

Two of the upper branches of the "hydrogen tree" deserve special consideration as prospective areas of growth. The fuels and the metallurgical applications for hydrogen could both expand very significantly into new uses of hydrogen, thus replacing the direct use of fossil fuels, which are in short supply. For example, replacement of large sectors of the industrial natural gas load with hydrogen produced from coal or from nonfossil sources would be easier to achieve than extensive electrification of industry. The use of nuclear-derived hydrogen as a direct reductant for iron and steel is under active consideration by the steel industry and could have a major impact on fossil-fuel use.

In considering hydrogen utilization in more detail, we shall discuss each major class of current hydrogen applications, quantitatively whenever possible; and we shall discuss the technological options for replacing the present source of hydrogen with a pipeline supply of hydrogen from an external, nonfossil-fuel source. The emphasis of this discussion will be on ammonia synthesis, methanol synthesis, hydrotreating, and hydrogenation (because they are major users) and on metallurgical and fuels applications (because they show the best prospects for revolutionary gains).

Hydrogen Utilization for Ammonia Production

Hydrogen feedstock for ammonia synthesis is currently prepared from hydrocarbon fluids, such as natural gas and naptha, and from coal or coke via reforming and/or partial oxidation processes. Hydrogen may also be

made from water and electrical power via electrolysis (of particular benefit where hydropower is cheap). Table 12-1 shows the worldwide trends during the 1960's for the production of hydrogen, from these several raw materials, for ammonia synthesis.

Table 12-1. FEEDSTOCK-HYDROGEN PRODUCTION FOR THE AMMONIA INDUSTRY
(World Average)

Source	1962	1967*	1969†
	wt %		
Natural Gas and Refinery Gas	41	57	62
Naphtha	--	11	15
Fuel Oil	11	5	5
Coal or Coke	37	21	14
Electrolytic	9	4	2
Others	2	2	2
Total	100	100	100

*Nitrogen No. 51, 1 (1968) January-February.

†Chem. Mark. Rep., 15 (1970) January 26.

In Table 12-1, the shift from the less desirable raw materials (coal, coke, and fuel oil) to the cleaner, more readily converted hydrocarbons (primarily natural gas and naphtha) is clear. During this 7-year period, electrolytic hydrogen declined from 9% to 2% of the total. In the United States, virtually all present ammonia production depends on natural gas as a feedstock. The rather rapid buildup in world capacity for synthetic ammonia production from 1967 to 1973 is shown in Table 12-2.

In the United States, ammonia production is concentrated in Louisiana and Texas (based on ready natural gas availability), along the Mississippi River and its major tributaries, and near the agricultural centers of use. Production of ammonia in 1974 totaled 15.7 million tons, with an expected annual growth rate through 1980 of 4.5%. Appendix A-3 lists all the major U.S. ammonia producers and their plant output capacity. The geographic distribution of these producers is shown in Figure 12-2. About 80% of the

Table 12-2. WORLD CAPACITY FOR SYNTHETIC AMMONIA*

	1967	1969	1973
	10^6 tons		
Western Europe	12.4	14.0	18.2
U.S.A.	11.3	14.6	16.4
Japan	2.7	3.0	4.8
Asia (Non-Communist)	2.2	3.0	8.1
Others (Including Communist Asia)	4.1	6.1	8.2
U.S.S.R.	3.9	5.8	7.5
Eastern Europe	3.5	6.2	8.0
Total	40.1	52.7	71.2

*Chem. Mark. Rep., 4 (1970) January 26.

ammonia produced is consumed directly as fertilizer or as an intermediate for fertilizer production.

To synthesize ammonia, nitrogen and hydrogen are combined in a 1:3 molar ratio at a high pressure and temperature in the presence of a catalyst:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

In current U.S. practice, hydrogen is derived from the steam reforming of natural gas, during which air is added to supply the required amount of nitrogen. Oxygen is removed by combustion with natural gas in a secondary reformer.

The amount of hydrogen required to produce 1 ton of ammonia can be calculated by dividing the hydrogen content of the ammonia by the overall yield of the synthesis step. One ton of ammonia contains 353 pounds (or 66,700 SCF) of hydrogen. Older processes claim a yield of from 85% to 90%. Most of the currently installed plants use the newer processes, such as M. W. Kellogg Co.'s process, which converts 96.7% of the synthesis gas to ammonia (which corresponds to a consumption of 78,500 SCF of hydrogen per ton of product ammonia).

When an ammonia plant is based on natural gas reforming, production of 1 ton of ammonia requires about 35,000 SCF of natural gas, of which 56% is used as feedstock and 44% is fuel. Today, an economical plant size is from 750 to 1000 tons/day; but a few 1500 ton/day plants have been built.

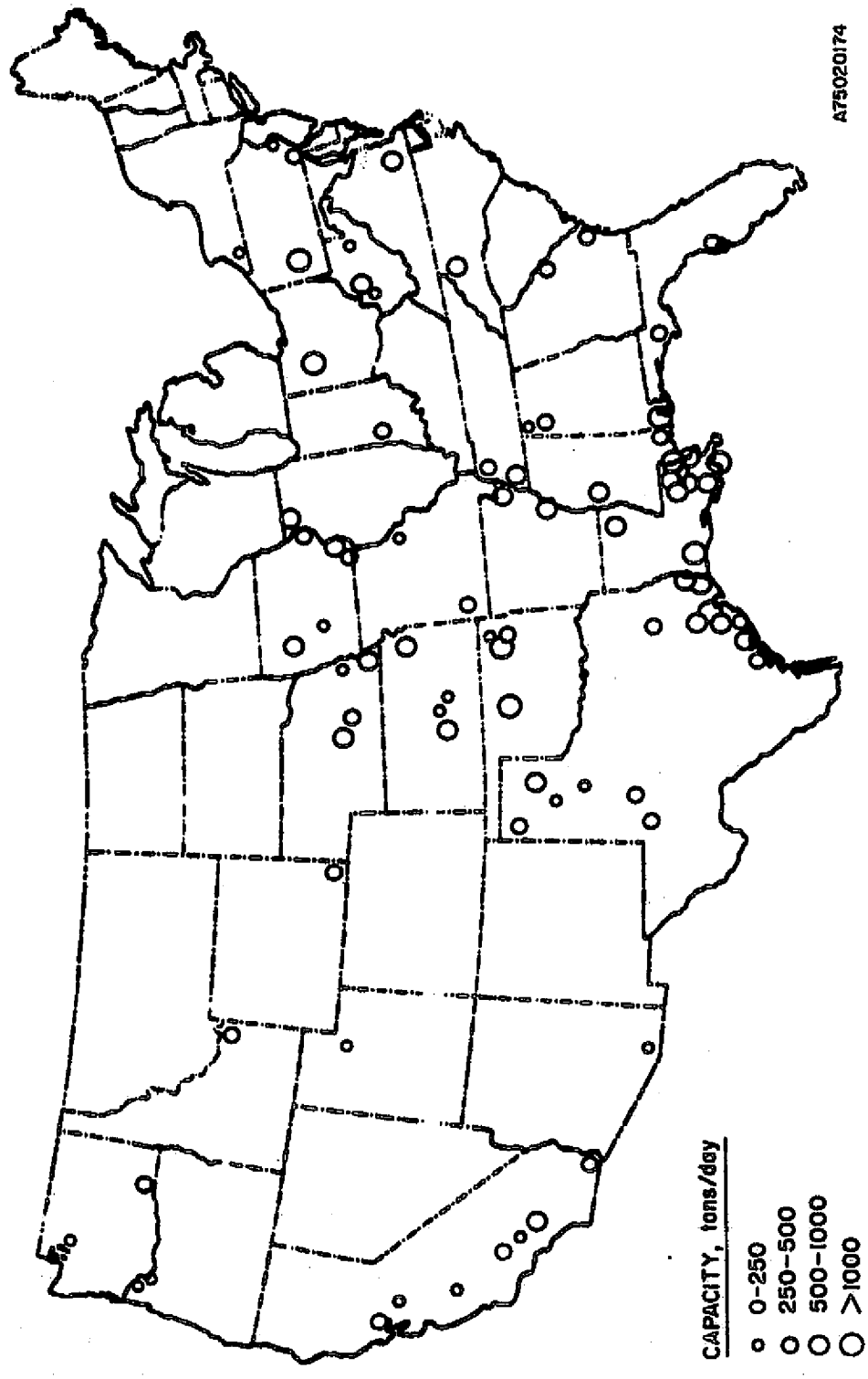

Figure 12-2. U.S. Ammonia Plants

The cost of hydrogen production is a significant percentage of the total ammonia-manufacturing cost. For this reason, the natural gas situation (i.e., its rising price and uncertain supply) is having a profound effect on U.S. ammonia production – ammonia prices having more than doubled within the last 18 months.

Ammonia Produced From Natural Gas

Figure 12-3 is a flow diagram for a typical ammonia-synthesis process, the CHEMICO Process (Chemical Construction Corp., New York). Other processes are those of the Tennessee Valley Authority, M.W. Kellogg Co., Societe Belle de l'Azote (SBA), Fauser, Casale, and Claude.[17] These processes are fundamentally equivalent in their conversion of natural gas, water, and air to ammonia; and their key by-products are carbon dioxide and waste heat. Any sulfur removed from the natural gas is either rejected as hydrogen sulfide or further converted to elemental sulfur.

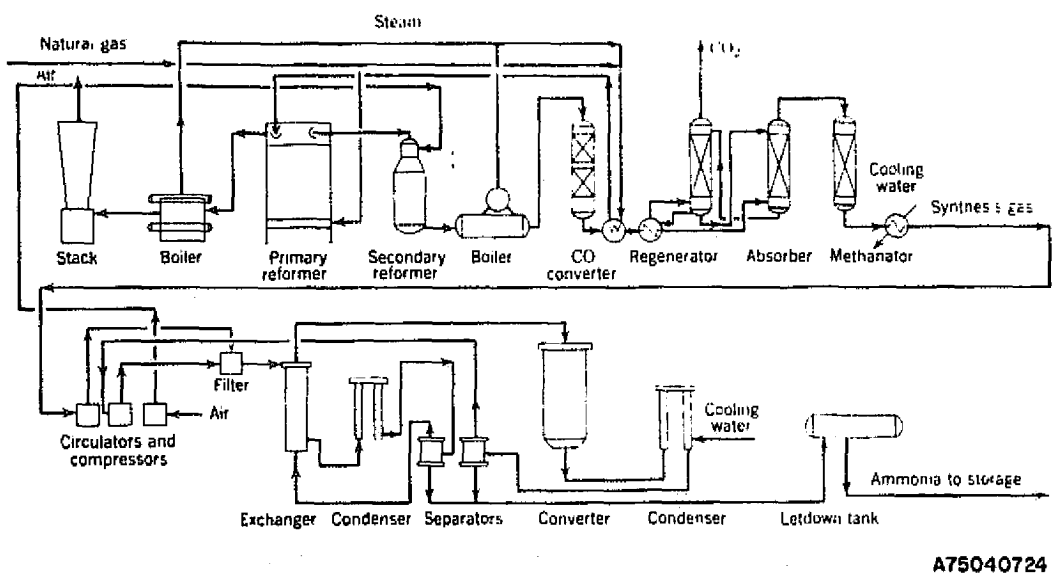

Figure 12-3. FLOW DIAGRAM OF A TYPICAL AMMONIA-SYNTHESIS PROCESS (CHEMICO Process)

The following six steps describe the plant's operation:

1. Natural gas and steam are combined in the primary reformer to produce hydrogen and carbon monoxide in a high-temperature catalytic, endothermic process.

2. The product gases are fed into a secondary reformer, into which a measured quantity of air is provided. The mixture is combusted with oxygen, leaving atmospheric nitrogen for synthesis gas makeup and small quantities of inerts such as argon.

3. After heat is extracted from the gas stream to produce steam (in the boiler), carbon monoxide and additional steam are shifted to hydrogen and carbon dioxide in the CO converter.

4. The carbon dioxide and remaining carbon monoxide are removed by chemical scrubbing. The remaining oxides of carbon are converted to methane in the methanator. These steps protect the ammonia synthesis catalyst from oxides of carbon. The concentrations of oxygen and all oxides must be reduced to very low levels (to approximately 5 ppm).

5. The resulting synthesis gas, consisting of nominally 75% hydrogen and 25% nitrogen (molar ratio), plus inerts (methane, argon, helium, etc.) and "contaminants" (carbon monoxide, carbon dioxide, water vapor, hydrogen sulfide, and oxygen) at suitably low levels, is then compressed from reformer pressure levels of from 500 to 750 psi to synthesis pressure levels. These usually range from 3000 psi to 4500 psi and even higher, requiring considerable energy expenditure for compression. Most of the compressor drive energy is provided by waste heat from the reforming operations. (The reforming reaction itself is endothermic, but not all the heat generated to drive the reforming steps is of high enough quality to be used to drive the reactions.)

6. The synthesis converter is basically a high-pressure vessel filled with a catalyst. Compressed synthesis gas is fed into the reactor in various ways, depending on the reactor's specific design. The synthesis reaction is exothermic, and the incoming synthesis gas is usually employed to cool the catalyst beds while effecting gas preheating. Water-cooled heat exchangers condense liquid ammonia out of the circulating synthesis gas stream. The product liquid ammonia is then passed through a letdown tank to storage.

Continuous venting of the synthesis vessel is necessary to preclude the buildup of inerts, which can significantly inhibit the conversion process. Losses associated with venting, which are significant, can be reduced by minimizing the concentrations of these inerts.

Ammonia Produced From Hydrogen Feedstock

Looking ahead to the possibility of large-scale ammonia synthesis directly from hydrogen (supplied, for example, via gas pipeline), one observes that the ammonia-synthesis facility must be rather drastically changed from the

baseline described above. The entire top line of Figure 12-3 — i.e., the "Stack" through the "Methanator" subsystems — is no longer required, but a new technique for deriving the nitrogen component of the synthesis gas will be necessary. The two possible approaches are 1) removal of oxygen from air by combustion of hydrogen-air mixtures and subsequent condensation of the resulting water vapor and 2) cryogenic air separation.

The first option, analogous to the use of natural gas in the secondary reformer, is not so wasteful of hydrogen as might at first be supposed. In the overall process, which approximates to —

$$1/2(O_2 + 4N_2)_{air} + 7H_2 \rightarrow 4NH_3 + H_2O$$

only one-seventh of the hydrogen is used to eliminate oxygen. This concept also eliminates the need for scrubbing out and venting the oxides of carbon. A hydrogen-air combustion system would probably be relatively simple and low cost and would also provide a source of heat for powering ancillaries such as compressors.

The second alternative, air-separation processes, are well established industrially for producing high-purity nitrogen. Of the existing large-quantity plants, the largest is Linde's (Division of Union Carbide Corp.) East Chicago facility, which produces 4200 tons of gaseous nitrogen and 5000 tons of gaseous oxygen per day. However, the air-separation process requires an energy input.

A conceptual schematic of an ammonia facility based on outside hydrogen is shown in Figure 12-4. Preliminary efficiency and product-cost comparisons for an ammonia plant fed by natural gas with one fed hydrogen are shown in Appendix A-4. Figure 12-5 shows the cost of ammonia as a function of the price of the hydrogen supplied.

More detailed analyses of the various options for producing ammonia from nonfossil fuels are required. Some work has already been done in this area. Experience with large-scale ammonia plants, for which hydrogen is supplied by hydroelectric-powered water electrolyzers, has been obtained in several countries.[8] (See Section 3.) The U.S. Army carried out extensive studies on the potential production of ammonia from nuclear electrolysis as

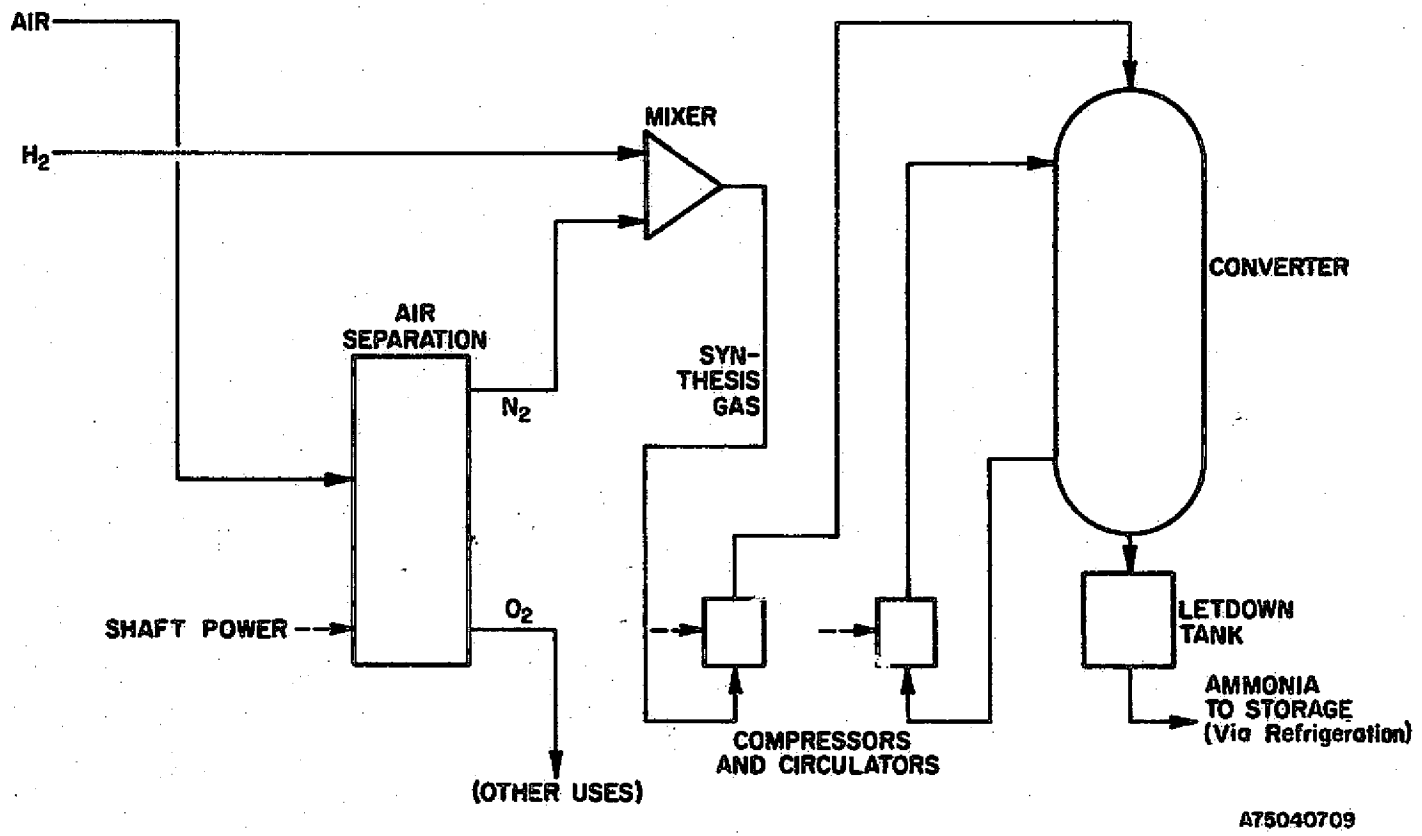

Figure 12-4. CONCEPTUAL FLOW DIAGRAM OF A HYPOTHETICAL AMMONIA-SYNTHESIS PROCESS THAT USES HYDROGEN FEEDSTOCK

part of the "Energy-Depot" concept.[9] Oak Ridge National Laboratory has studied the production of ammonia from nuclear energy in the "Argo-Industrial-Complex" concept.[4]

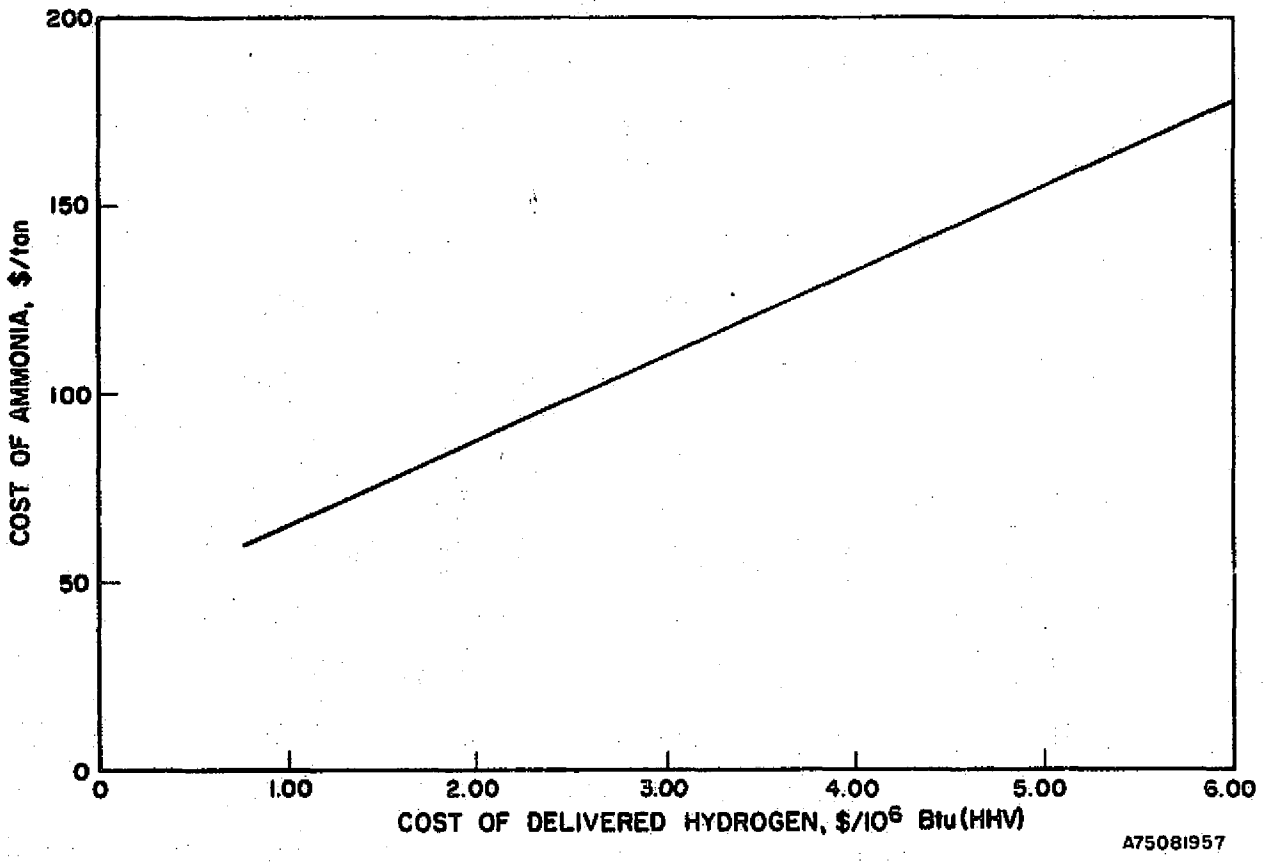

Figure 12-5. COST OF AMMONIA VERSUS COST OF DELIVERED HYDROGEN FOR A PRODUCTION FACILITY THAT USES OUTSIDE HYDROGEN

Hydrogen Utilization for Methanol Production

In industry, methanol is used as a solvent and as a raw material, mainly for the production of formaldehyde, synthetic resins, dye stuffs, and related chemical products. Table 12-3 reflects world methanol-production capacity in 1968 and 1970, exclusive of the U.S.S.R. and Eastern Europe. As seen in the table, the United States, Japan, and the Western European nations are the principal producers.

Table 12-3. WORLD METHANOL-PRODUCTION CAPACITY*
(Excluding the U.S.S.R. and Eastern Europe)

	1968	1970
	10^6 gal/yr	
U.S.A.	650	1035
Japan	380	680
West Germany	250	340
United Kingdom	120	135
Italy	85	100
France	70	70
Canada	30	40
The Netherlands	30	30
Australia	15	20
Others	90	100
Totals	1720	2550

*Conversion factors: 6.63 pounds of methanol per gallon (at 20°C), 10^6 gal/yr = 3000 tons/yr.[10]

In the United States, methanol production is sited largely in areas of ready accessibility to natural gas — mainly along the Gulf Coast. The major U.S. methanol plants are listed in Table 12-4, and their locations are shown in Figure 12-6.

In 1973, the U.S. produced 960 million gallons (or 3,180,000 tons) of methanol. Because 26 SCF of hydrogen is required per pound of methanol produced,* the total hydrogen requirement is 165 billion SCF. Since 1962 the annual growth rate has been 10%, but it is expected to be somewhat less in the future. (The growth rate was 7.8% in 1973-74.)

Methanol is synthesized from a gas (Syngas) that consists of hydrogen and carbon monoxide in a molar ratio of 2:1. The synthesis reactions is —

$$CO + 2H_2 \rightarrow CH_3OH$$

The synthesis is usually performed over a zinc-chromium or copper-zinc catalyst at a temperature of from 250° to 300°C and at 500 to 5000 psi. Low-pressure processes are also available, and these are claimed to be economically attractive.[1]

* Some sources claim a requirement of up to 37 SCF/lb.

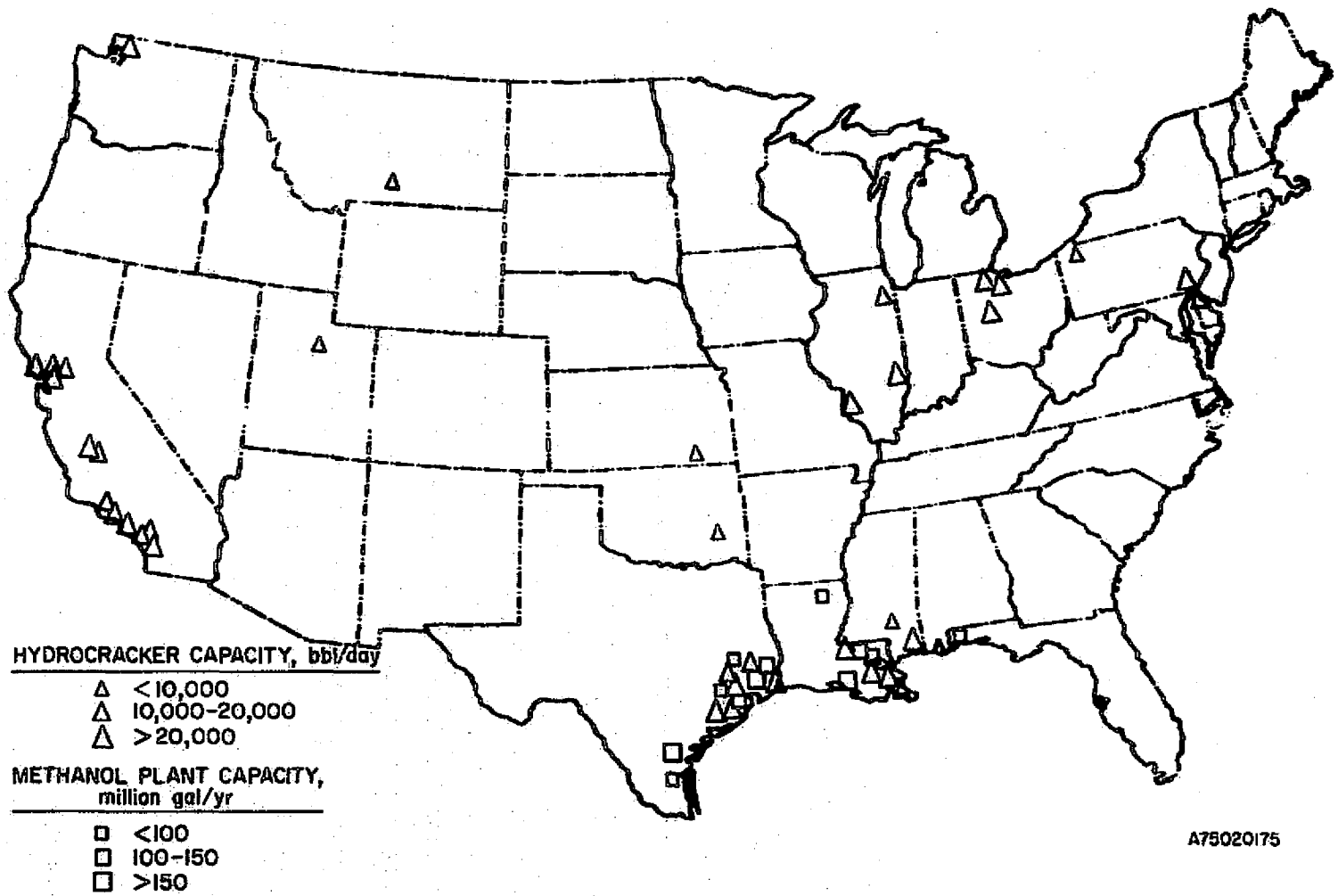

Figure 12-6. U.S. METHANOL PLANTS AND HYDROCRACKING FACILITIES

Table 12-4. U.S. METHANOL PLANTS*

Producer	Capacity, 10^6 gal/yr
Air Products and Chemicals, Inc. Pensacola, Fla.	50
Borden Chemical Div., Geismer, La.	160
Celanese Corp., Bishop, Tex.	50
Celanese Corp., Clear Lake, Tex.	230
Commercial Solvents Corp., Sterlingten, La.	50
E.I. du Pont de Nemours & Co., Inc. Orange, Tex.	100
Georgia-Pacific Corp., Plaquemine, La.	100
Hercules Inc., Plaquemine, La.	100
Monsanto Co., Texas City, Tex.	100
Rohm & Haas Co., Deer Park, Tex.	22
Tenneco Inc., Houston, Tex.	80
Total Capacity	1042

* "Chemical Profile: Methanol," Chem. Mark. Rep. 205, 9 (1974) June 17.

The synthesis train basically resembles that of ammonia production (Figure 12-3) with certain obvious differences:

a. Carbon monoxide conversion in the shift reaction is carried only to the point of establishing the 2:1 molar ratio.

b. Nitrogen is not required and, in fact, is undesirable in the hydrocarbon feedstock.

c. A special methanol-synthesis reactor is required.

Methanol Syngas can be obtained from any reforming or partial-oxidation process that uses a natural gas or oil feedstock or from coal. Also, the off gases from a basic oxygen furnace (BOF) for steel can be used as a feedstock for methanol synthesis. However, even the largest BOF installations produce only enough carbon monoxide to make 25 million gallons of methanol per year; and this rate of production is too small, by today's production standards, for such a plant to be economical.

The outlook for a methanol-synthesis plant that uses an outside supply of hydrogen is not as promising as in the case of ammonia synthesis. The requirement for a major source of carbon oxides is most easily satisfied by

hydrocarbon feedstocks (which are reformed) or by coal. On the other hand, an outside pure-hydrogen source could make the use of BOF gas more competitive by eliminating the water shift reaction, which sacrifices carbon monoxide to obtain hydrogen.

Hydrogen Use in Oil Refining

The following quotation from a late-1973 U.S. Bureau of Mines commodity statement for hydrogen[18] is instructive in regard to hydrogen usage in refining.

> "In petroleum refining, hydrocracking is the most significant development with regard to hydrogen consumption. Hydrocracking is used to raise the hydrogen-carbon ratio of the heavier, high-boiling hydrocarbons. For example, lower value heavy fuel oils can be upgraded into more valuable lighter fractions, such as gasoline, light heating fuel oil, and diesel fuel oil, at the same time effecting savings in refining costs.
>
> "Raising the hydrogen/carbon ratio, as outlined above, requires copious amounts of hydrogen. For each barrel of charging stock, between 2,500 and 2,700 cubic feet of hydrogen are used. As of the end of 1972, hydrocracking capacity had expanded to about 865,000 barrels per stream day. During 1972, it is estimated that 800 billion SCF of hydrogen was used in hydrocracking, or 2.2 billion cubic feet per day. Between 1965 and 1972, hydrogen consumption for hydrocracking increased eight fold, from 100 to 800 billion SCF. Based on expansion plans, hydrocracking promises to become the largest consumer of hydrogen in the United States.
>
> "Hydrotreating, the much older use for hydrogen in petroleum refining, consumed 570 billion SCF in 1972. In hydrotreating, hydrogen is reacted with refinery fractions to desulfurize feedstocks. Hydrogen is used to hydrogenate olefins and to treat lubricating oils and kerosine-type jet fuels. The growth in hydrotreating has been coincidental with the introduction of catalytic reforming, a process widely used for octane upgrading of motor-gasoline components. The net result of catalytic reforming is a hydrogen production equal to 1.5 times input. The hydrogen used in hydrotreating is that present in the off gas from a catalytic reforming unit. Since hydrotreating required a maximum of 300 cubic feet per barrel of feed, only part of the hydrogen content of the gas is consumed. The exit gas, still containing 70% to 75% hydrogen along with hydrogen sulfide generated by the hydrotreating process, is used as fuel."

It is extremely difficult to estimate the net consumption of hydrogen in refinery operations because the processes in most refineries are both consumers and producers of hydrogen. The net effect depends on the refinery process design, the composition of the crude being processed, and the product mix required. Refineries with a net deficit of hydrogen currently obtain supplies by steam reforming natural gas or naphtha. In general, only refineries with hydrocracking facilities require a net input of hydrogen. Refineries of this type are listed in Table 12-5; and their locations, primarily along the Gulf Coast and in California, are shown in Figure 12-6.

Table 12-5. U.S. REFINERIES WITH HYDROCRACKING PROCESSES[6]

Company	Location	Capacity Charged to Hydrocracker, bbl/stream day
California		
Atlantic Richfield Co.	Carson	19,700
EXXON Co., U.S.A.	Benecia	22,000
Gulf Oil Corp.	Santa Fe Springs	11,000
Mobil Oil Corp.	Torrance	18,000
Phillips Petroleum Co.	Avon	22,000
Shell Oil Co.	Martinez	19,000
Standard Oil Co. of Calif.	Bakersfield	49,000
Standard Oil Co. of Calif.	Richmond	67,500
Texaco Inc.	Wilmington	20,000
Toscopetro Corp.	Bakersfield	13,300
Union Oil Co. of Calif.	Los Angeles	21,000
Union Oil Co. of Calif.	San Francisco	30,000
Delaware		
Getty Oil Co.	Delaware City	17,000
Illinois		
Clark Oil & Refining Corp.	Blue Island	11,000
Marathon Oil Co.	Robinson	22,000
Shell Oil Co.	Wood River	33,500
Kansas		
Apco Oil Corp.	Arkansas City	2,950
Louisiana		
EXXON Co., U.S.A.	Baton Rouge	21,000
Gulf Oil Co.	Venice	11,500
Shell Oil Co.	Norco	28,000
Tenneco Oil Co.	Chalmette	18,000
Mississippi		
Amerada Hess Corp.	Purvis	3,000
Standard Oil Co., of Ky.	Pascagoula	59,000
Montana		
EXXON Co., U.S.A.	Billings	4,900
Ohio		
Standard Oil Co. of Ohio	Lima	20,000
Standard Oil Co. of Ohio	Toledo	36,000
Sun Oil Co.	Toledo	26,000
Oklahoma		
Kerr McGee Corp.	Wynnewood	4,500
Pennsylvania		
Atlantic Richfield Co.	Philadelphia	30,000
Pennzoil Co.	Rouseville	2,700
Texas		
Amoco Oil Co.	Texas City	38,000
Atlantic Richfield Co.	Houston	4,500
EXXON Co., U.S.A.	Baytown	20,000
Gulf Oil Corp.	Port Arthur	15,000
Mobil Oil Corp.	Beaumont	29,000
Shell Oil Co.	Deer Park	25,000
Texaco Inc.	Port Arthur	15,000
Union Texas Petroleum, Div.	Winnie	3,000
Utah		
Caribou Four Corners, Oil Co.	Woods Cross	1,000
Washington		
Atlantic Richfield Co.	Ferndale	35,000

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The outlook for hydrogen use in refineries is mixed. Refineries are facing increasingly strict sulfur-emissions standards and at the same time are being called upon to process products from less desirable types of crude oil. Consequently, in the last 2 years hydrotreating has grown at an annual rate of 10%, with capacity additions planned in 1975 at an even higher rate. On the other hand, hydrocracking growth has virtually come to a halt, with only nominal additions planned for 1975.[11]

The approximate ranges of hydrogen requirements per barrel of feed charged for various processes are shown in Table 12-6.

Table 12-6. HYDROGEN-REQUIREMENT RANGES

Process	Hydrogen Requirement, SCF/bbl
Hydrotreating Reformer Feed	65-150
Desulfurization	
Light gas oil	85-180
Heavy gas oil	380-500
Residual fuel oil	500-1200
Hydrocracking	1800-2500
Catalytic Reforming	+600-800 (Hydrogen produced)

These figures can be used to estimate hydrogen use in refineries, as shown in Table 12-7.

Table 12-7. REFINERY HYDROGEN USAGE

	1973 Charge,[11] bbl/stream day	% of Total Crude Charged	Ratio SCF/bbl	1973 Hydrogen Use, 10^9 SCF
Hydrotreating	5,780,110	39	270	542
Hydrocracking	855,840	8.5	2500	742
Total Hydrogen Demand				1284
Catalytic Reforming	3,358,038	22	700	815
Net Hydrogen Deficit				469

Metallurgy

Small quantities of merchant hydrogen are used in specialty metallurgical processing (including the production of very pure metals) and for the production of certain nonferrous metals (including tungsten, molybdenum, and

tantalum). Larger quantities of captive hydrogen, usually impure and produced onsite, are used for inert or reducing atmospheres in heat-treating applications. Even larger quantities of hydrogen, in the form of blast-furnace gases, are used indirectly in the conventional reduction of iron ore (although carbon is the primary reducing material involved).

Direct Reduction of Iron Ore

There is tremendous potential for a new increased use of hydrogen, or of hydrogen-carbon monoxide mixtures, in the direct reduction of iron ore. The direct-reduction process produces "sponge iron," which is then used as a feed for steelmaking in an electric-arc furnace. Direct-reduction processes are attractive where coal is not readily available and hydrocarbon feedstocks for the hydrogen-carbon monoxide reductant stream are inexpensive and plentiful. An added incentive is that long-distance transportation of sponge iron is less expensive than moving iron ore, coal, or natural gas. Thus, direct-reduction processes have been utilized primarily in the "petroleum-rich" countries. In the United States, however, natural gas supplies are declining; costs are rising; and there is now incentive to investigate the potential for operating a direct-reduction process on an independent (non-fossil) hydrogen supply.

After 10 to 15 years of development, almost a dozen direct-reduction processes, with a variety of features, have been made commercially available. As shown in Table 12-8, one basic characteristic by which available processes can be classified is the type of reaction bed employed.

Table 12-8. CLASSIFICATION OF DIRECT-REDUCTION PROCESSES BY REACTION-BED TYPE[12]

Type of Reaction Bed	Representative Direct-Reduction Process
Vertical fixed	Hojalata y Lamina, S.A. (HYLSA)
Vertical-shaft, moving	Midrex Corp., Armco Steel Corp., Thyssen Purofer GmbH
Rotary-kiln	Steel Co. of Canada, Ltd.; Lurgi Chemie und Huttentechnik; Republic Steel Corp.; NL Industries, Inc.; Fried. Krupp GmbH; Allis-Chalmers Corp.

As of 1974, more than 11 million metric tons of metallized product were produced worldwide, the bulk of which was used in electric-arc furnaces for steelmaking.[16] Currently, the capacity of the direct-reduction plants in operation and on order totals 19 million tons of metal per year. An additional capacity of 2.8 million metal tons is in the "letter-of-intent," "advanced-planning," or "under-study" stage.[20]

Because a substantial treatment of the broad field of direct reduction of iron ore is not possible within the scope of this study on industrial hydrogen usage, the remainder of this section focuses only on iron-ore reduction with hydrogen.

Direct Reduction via Hydrogen

The "H-Iron" Process, developed by Hydrocarbon Research Inc. (HRI) in collaboration with the Bethelehem Steel Co., is a method for producing iron by direct reduction of iron ore with hydrogen. Finely divided ore is reduced in fluidized beds at temperatures below 1000°F and at pressures above 200 psig. The process resulted from efforts, in about 1950, to produce iron-based catalysts for refinery use. Developments proceeded to 50 and 183 tons/day plants in 1960 and 1961, respectively.[7]

Figures 12-7 and 12-8* are, respectively, schematic diagrams of the solids and gas circuits for the "H-Iron" Process. Hydrogen is produced in the process by steam reforming of natural gas, though other fossil and non-fossil sources are also acceptable. Conventional equipment is used to dry and grind the ore, and the ore is preheated to remove contaminants.

A sequenced batch process is used. Powdered ore, loaded into the charge hopper, is first purged of air and then pressurized (with hydrogen) to 150 psi above reduction pressure. The ore is then "pressure transferred" (fluidized) to the first of three reducing sections. Progressive reduction occurs in the hot hydrogen stream as the batch sequence proceeds. Basically, this conserves hydrogen by accomplishing a more complete reduction per pass. From the dump hopper, the metallized product, consisting of elemental iron (nominally 95% reduced) and accompanying gangue, (the worthless rock that surrounds the iron ore vein) is placed in storage. From there it can be directly utilized in the steelmaking process.

*Adapted from sketches in "Economics of Primary Iron and Steel Production in the West Coast From Local Iron Ores Via the 'H-Iron' Direct-Reduction Process."[7]

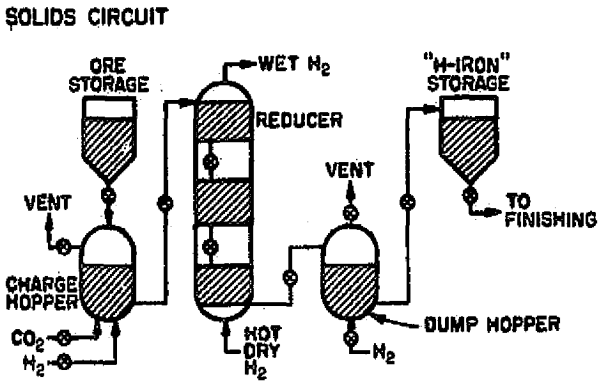

Figure 12-7. DIRECT IRON ORE REDUCTION WITH HYDROGEN VIA THE H-IRON™ PROCESS

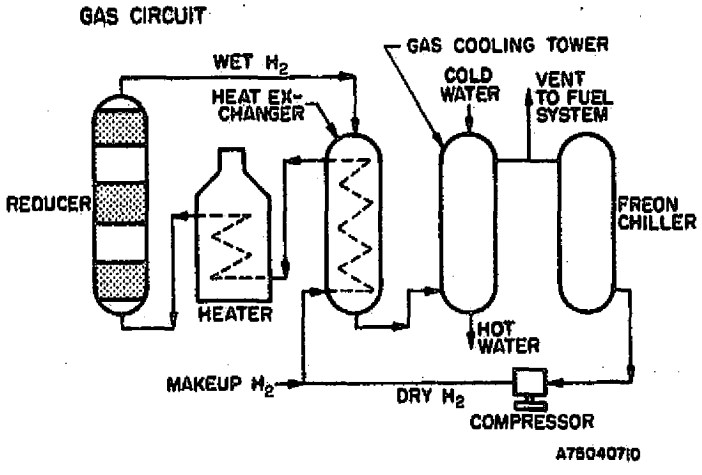

Figure 12-8. GAS CIRCUITS IN THE H-IRON™ PROCESS

The hydrogen reductant circulates in the process, as shown in Figure 12-8. It is preheated in a heat exchange with spent (i.e., "wet") reductant and is then reheated to reduction temperature (about 1000°F), following which it is routed through the reducer. Water is formed during the reduction of iron ore. This is removed from the spent stream by simple condensing processes using water and freon. The dry hydrogen is compressed, makeup hydrogen is added, and the cycle is repeated.

Although demonstrated to be technically feasible by the early 1960's, direct hydrogen reduction has had very limited application to date because of unfavorable market forces in steelmaking. Based on an IGT query to HRI, one of the few "H-Iron" facilities in operation profitably converts mill-scale (basically pure) iron oxide to a very refined metallized product that is used in welding-rod manufacturing, molding powders, and other powered metallurgy products.

Iron and steel industry representatives show an increasing interest in the potential for using nuclear energy directly in steelmaking. This growing interest in "nuclear steelmaking" has recently come to the fore in the United States, Japan, and Europe and may serve to reawaken interest in direct hydrogen reduction.

The American Iron and Steel Institue (AISI) has established the "Task Force on Nuclear Energy in Steelmaking." This is chaired by Donald J. Blickwede, Director of Research, Bethlehem Steel Corp. Mr. Blickwede and T. F. Barnhart, of U.S. Steel Corp., presented an informative paper in late 1974, "The Use of Nuclear Energy in Steelmaking – Prospects and Plans."[15] In this paper, several modes of employing nuclear process heat were surveyed; and their economics where assessed on both industrial- and utility-financing bases. Fossil fuels were generally employed as sources of hydrogen and carbon monoxide mixtures.

Direct hydrogen reduction was considered in one of the cases examined. In this instance, no fossil fuel was used; and nuclear electrolysis was the method of hydrogen production. Figure 12-9* shows one of the results – the incremental effect of liquid steel on selling price as a function of the costs of both coking coal and "fossil fuels alternatives," with a reference case being coal at $20/ton (the dashed lines).

The top line in Figure 12-9, "Electrolysis-Utility Financing," is the abovementioned case that uses no fossil fuel (hence the slope of zero). However, it is clear that, for the conditions studied, fossil-fuel costs must significantly escalate for this electrolytic-hydrogen case to become competitive.

*Adapted from "The Use of Nuclear Energy in Steelmaking – Prospects and Plans."[5]

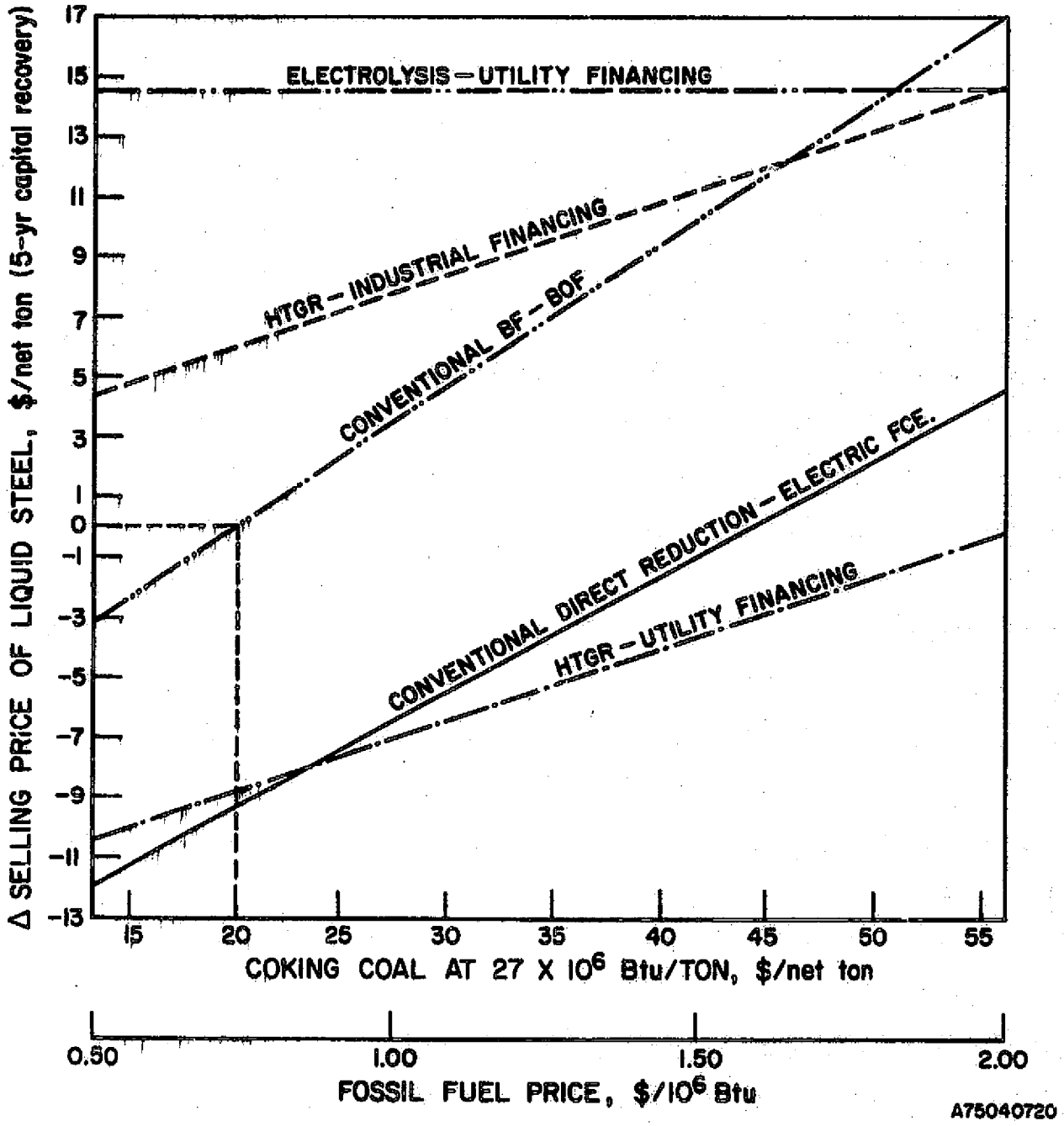

Figure 12-9. EFFECT OF FOSSIL-FUEL PRICE ON STEEL PRICE
(Source: D. J. Blickwede and T. F. Barnhart, 1974)

IGT asked Mr. Barnhart for his opinion on the technical prospects for direct hydrogen reduction versus "conventional" direct reduction. (His paper pointed out a number of technical problems in the pure-hydrogen approach.) Mr. Barnhart offered the following observations and provided sources of additional information and a list of patents on hydrogen reduction.[2] (See Table 12-9.)

> "One of the principal difficulties in the hydrogen reduction of iron ore is the tendency for the reduced product to agglomerate in the reduction vessel. This has necessitated reduction at rather low temperatures, which in turn affect the productivity of the unit. Most of the work conducted by HRI was at temperatures in the neighborhood of 800° to 1000°F, which is considerably below that used in a modern direct-reduction shaft where the reducing gas may be 1400° to 1600°F. A second problem is the pyrophoric properties of the product, which in the past [have] necessitated annealing so that the material could be safely handled. Because of these difficulties and because of the success of the present direct-reduction plants, there has been little incentive for the steel industry to pursue hydrogen reduction. Therefore, there has been very little work conducted in the last decade on this subject."

He made the point, however, that such technical problems would likely be overcome if hydrogen became available at a competitive price.

Table 12-9. U.S. PATENTS RELATING TO DIRECT REDUCTION OF IRON ORE WITH HYDROGEN

Patent No.	Title	Assignee	Date
3,140,040	Iron Oxide Reduction With Hydrogen	Keith, P.C.	July 14, 1964
3,154,405	Reduction of Iron Oxide	Engle, T.M. et al.	October 27, 1964
3,224,869	Method of Reducing Iron Oxide	Keith, P.C. et al.	December 21, 1965
3,224,870	Reduction of Ilmenite and Similar Ores	Johnson, C.A. et al.	December 21, 1965
3,227,546	Direct Reduction of Metallic Ores	Johnson, C.A. et al.	January 4, 1966
3,257,198	Beneficiation of Ore	Volk, W. et al.	June 21, 1966
3,347,659	Process of Reducing Iron Oxide	Volk, W. et al.	October 17, 1967
3,383,200	Reduction of Metallic Oxides	Volk, W.	May 14, 1968
3,414,402	Beneficiation of Low-Grade Iron Ores	Volk, W. et al.	December 3, 1968

Use of Hydrogen as an Industrial Fuel

Present Use

At present, hydrogen is used as an industrial fuel only under special circumstances — for example, when an unwanted by-product stream of low-pressure or impure hydrogen is available from a nearby chemical process. Many industrial operations recover the fuel value of this by-product by using it directly as a boiler fuel. In some isolated cases, hydrogen has been considered as a space-heating fuel.

Although this use of hydrogen is extremely limited at present, its potential for growth is enormous. Until now, we have considered only chemical-feedstock uses for hydrogen. The entire use of energy resources for chemical feedstocks accounts for only about 5% of U.S. consumption. On the other hand, industrial-fuel uses account for about 27% of the total consumption. It is therefore in this area that the greatest potential for industrial hydrogen utilization lies.

Before considering the future potential of hydrogen for fuel use, we investigated some of the factors influencing the present use of hydrogen as an industrial fuel. We visited North American Manufacturing Co., Cleveland. North American, a principal U.S. industrial gas- and oil-burner supplier, designs and assemblee components into fuel-air supply systems for industrial-process heat devices such as boilers, reactors, and melting furnaces. The company has processed about a dozen hydrogen-burner installations to date and anticipates an increase in this business.

In all hydrogen systems to date, North American has provided engineering services and has procured hydrogen-qualified components. However, final "piping up" was done by the customer. North American has supplied hydrogen-gas-train systems to the following concerns (presumably not an all-encompassing list):

Humko Products Div., Memphis
Hercules Powder Co., Hopewell, Va.
Bethlehem Foundry and Machine Co., Bethlehem, Pa.
J. T. Thrope and Co., Houston
Diamond Shamrock Corp., Paynesville, Ohio
Hooker Chemical Co., Buffalo
Goodyear Tire and Rubber Co., Akron (engineering only)

Hydrogen supply pressures of up to 15 psig and supply pipe sizes of up to 6 inches have been specified by the customers. Purity, in general, was "reasonably high"; but details were not given.

North American's comments on the use of hydrogen as a fuel centered mainly on the safety aspects and on the codes of practice, not on the design and operation of the burners or of the heating equipment itself.

North American uses special "precautions" in specifying the designs and component makeup of a hydrogen system. Electrical components for hydrogen service are under a different national electric code (Article 500 class) than those for use with other gaseous fuels (which are specified as "Class 1" by the code):

- Group A — atmospheres containing acetylene
- Group B — atmospheres containing hydrogen or gases or vapors of equivalent hazard, such as manufactured gas
- Group C — atmospheres containing ethyle-ether vapors, ethylene, or cyclo-propane
- Group D — atmospheres containing gasoline, hexane, naphtha, benzene, butane, propane, alcohol, acetone, benzol, laquer-solvent vapors, or natural gas.

Not many component vendors have equipment approved or listed by Underwriters' Laboratories for Class B service, which encompasses hydrogen.

According to representatives of North American, because of the liability of the company in cases of mishap involving equipment delivered to the customer, extreme precautions are considered appropriate. Specifically, the approval and/or recommendations of either (or both) Factory Insurance Agency (FIA) or Factory Mutual Engineering (FME), both of which provide regional-area cognizance, is strictly adhered to — and especially so for hydrogen service. Further, they noted that technical opinions provided by these groups vary from region to region.

Although not necessarily in agreement on their specifications/recommendations, representatives of the FIA and FME have called for an identical "minimum-system" layout for hydrogen gas trains. North American's interpretation of this specification is shown in Figure 12-10. This governs the basic layout of their hydrogen systems. A letter[13] from a representative of the local FME office to North American on the "Use of Hydrogen as a Fuel"

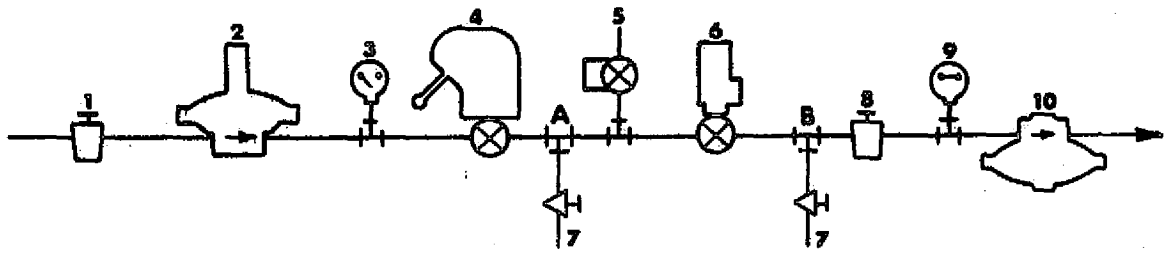

Figure 12-10. SCHEMATIC OF A GAS TRAIN FOR INDUSTRIAL BURNERS THAT USE HYDROGEN FUEL
(Source: North American Manufacturing Co.)

(High and low gas pressure limit switches must be downstream from the high gas pressure regulator. Equipment should be arranged in this order: (1) manual valve, (2) high gas pressure regulator, if used, (3) low gas pressure switch, (4) safety valve, (5) vent valve, (6) blocking valve, (7) leak test cock, (8) manual valve, (9) high gas pressure switch, and (10) ratio regulator, if used.)

is most instructive in view of the dominant influence of the FIA/FME organizations on the design and engineering of any future industrial equipment that uses hydrogen as a fuel:

> "Combustion safety equipment should, in general, be installed as per Factory Mutual standards for the particular piece of equipment if natural gas were being fired. One exception to this is that due to the low molecular weight and resulting high leakage potential of hydrogen, we recommend that a double safety shutoff valve and normally open vent assembly be used in the fuel supply line. Main burner trial for ignition periods should be limited to a maximum of 10 seconds. Requirements for pre-ignition purge should comply with existing Factory Mutual standards, but it is felt especially important that the purge involve the upper passes of the unit due to the light weight of hydrogen.
>
> "If the hydrogen is produced at the plant, it should, or course, be of high quality in regards to being free from air or oxygen. Piping at the burner should be arranged with as short a length of pipe as possible between the safety shutoff valve and the burner in order to minimize the possibility of a combustible hydrogen-air mixture forming in the piping during shutdowns. Premixing of the hydrogen with air should be avoided due to the fact that no flame arrester is completely effective under all conditions with hydrogen.
>
> "The selection of safety equipment, valves, pressure switches, etc., presents another problem. I feel that the combustion safeguard itself should be a Factory Mutual approved model. Flame detection may be a

problem, but we understand that ultra-violet scanners have been used successfully. Perhaps a reputable manufacturer of combustion safeguards could be of assistance.

"As for the remainder of the combustion safety equipment, I have been informed that no valves, pressure switches, etc., are approved by Factory Mutual for use with hydrogen. This is not to say that they could not be used with success, just that they have not been tested by Factory Mutual for this service. Accordingly, we can make no recommendation for the use of Factory Mutual approved equipment. We would, of course, recommend that good quality equipment be used and that manufacturers of the equipment be consulted regarding its use. It is likely that North American has data concerning appropriate valves for use with hydrogen, and perhaps a reputable manufacturer of pressure switches could give you advice in that area."

Potential Use

Industrial and electrical-utility usage of energy resources in the United States accounts for over one-half of the total energy usage. Figure 12-11 presents the basic breakdown, by percent, of the total U.S. energy usage. "Process energy" is approximately 32% of this total, heating fuels represent 28%, and electrical power from utilities comprises 9%.[15] An additional 4% of the total is used for feedstock purposes.

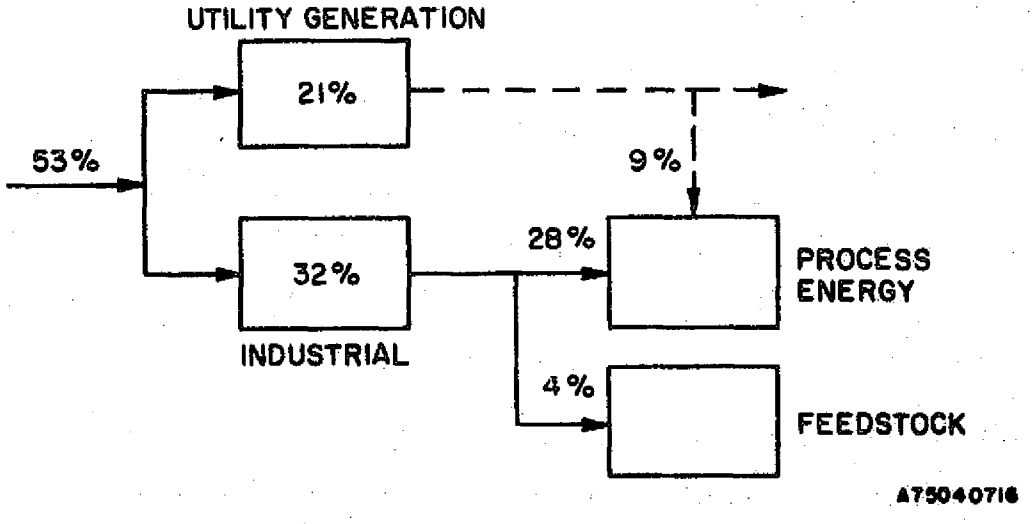

Figure 12-11. INDUSTRIAL AND UTILITY ENERGY USAGE

Figure 12-12 is a breakdown of the "process-energy" usage into steam (17.4%) and direct heat (10.9%). Note that industry generates only a relatively small amount of its consumed electricity, 0.7% as compared with the 9.3% purchased from utility companies.

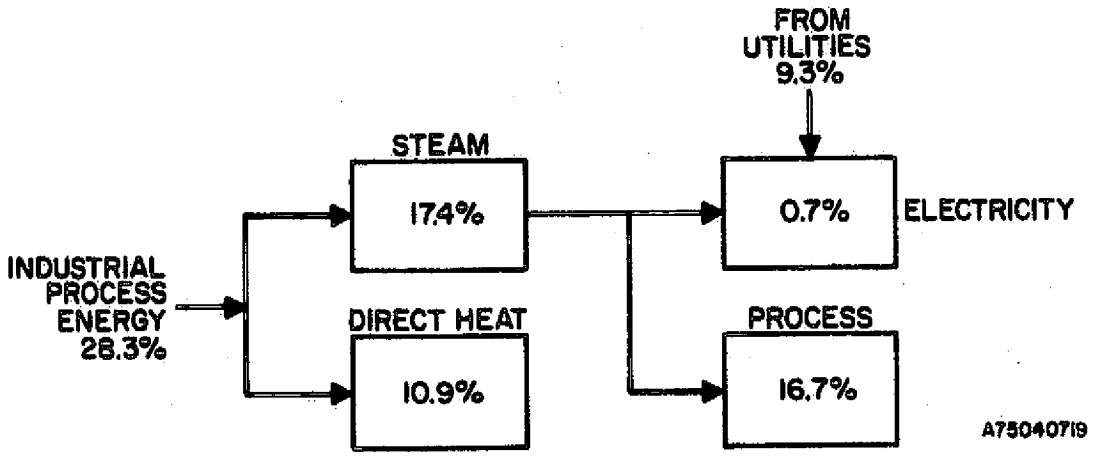

Figure 12-12. INDUSTRIAL-PROCESS-ENERGY COMPONENTS

Industrial energy needs are currently filled by natural gas (51%), oil (27%), and coal (22%). Preference is placed on natural gas because it is a clean, flexible, gaseous fuel. Significantly, hydrogen has the potential of providing these same advantages over liquid and solid fuels. The largest single industrial use of energy is for the generation of process steam. The energy consumed for this function, alone, is roughly equivalent to the total energy consumed by all automotive transportation (i.e., cars, trucks, and buses) in the United States.

The process-steam application deserves primary consideration for conversion to hydrogen utilization. Currently, about half of the energy used to provide process steam is delivered as natural gas. The conversion of conventional natural-gas-fired steam boilers to hydrogen could probably be accomplished with little modification of the conventional equipment. With

development and oxygen availability, hydrogen-oxygen direct steam-generation systems may be an environmentally clean, low-cost, flexible, and compact source of process steam at a wide range of temperatures.

This unique approach to steam generation, direct hydrogen-oxygen combustion at stoichiometric conditions, yields steam at extremely high temperatures. The calculated adiabatic flame temperature (and thus the steam temperature) is approximately 6000°F. Water would be added immediately to cool the steam to the desired temperature. The mass flow of steam is commensurately increased. The technology for this process is derived from rocket-engine development in the aerospace field.

Industrial firms, such as the Rocketdyne Division of Rockwell International Corp., and the General Electric Co., have carried out research on this type of steam generation for the past several years. Usually the objective has been associated with electricity generation using high-temperature-steam turbines. For example, General Electric refers to the scheme as "Hydrogen-Oxygen Turbine, Super-High Operating Temperature (HOTSHOT)."[14] Interestingly, the original patent for an "Oxyhydrogen Steam Generator" was issued to E. E. Tucker in 1924 (Patent 1,483,917). Actually, the hydrogen-oxygen steam process can be employed for any steam requirement, given an economic source of hydrogen and oxygen. Prospective advantages of this process over conventional boilers are –

a. Higher conversion efficiency (no stack losses, minimal heat losses)
b. No environmental pollution (zero emissions)
c. Lower cost equipment that is simple and long-lived
d. Instant start-up and shutdown
e. Temperatures much higher than can be produced conventionally.

Figure 12-13 shows the estimated competitive position of hydrogen steam generation in the overall U.S. nuclear and fossil-fuel system. The flatness of the hydrogen curve suggests the feasibility (via the hydrogen-oxygen approach) of very small, efficient, hydrogen-fueled steam generators. The arrow indicates anticipated improvements in efficiency and feasible cost reductions for hydrogen systems. As a point of perspective, contemporary industrial steam may cost upward of $3.00/1000 pounds.[21]

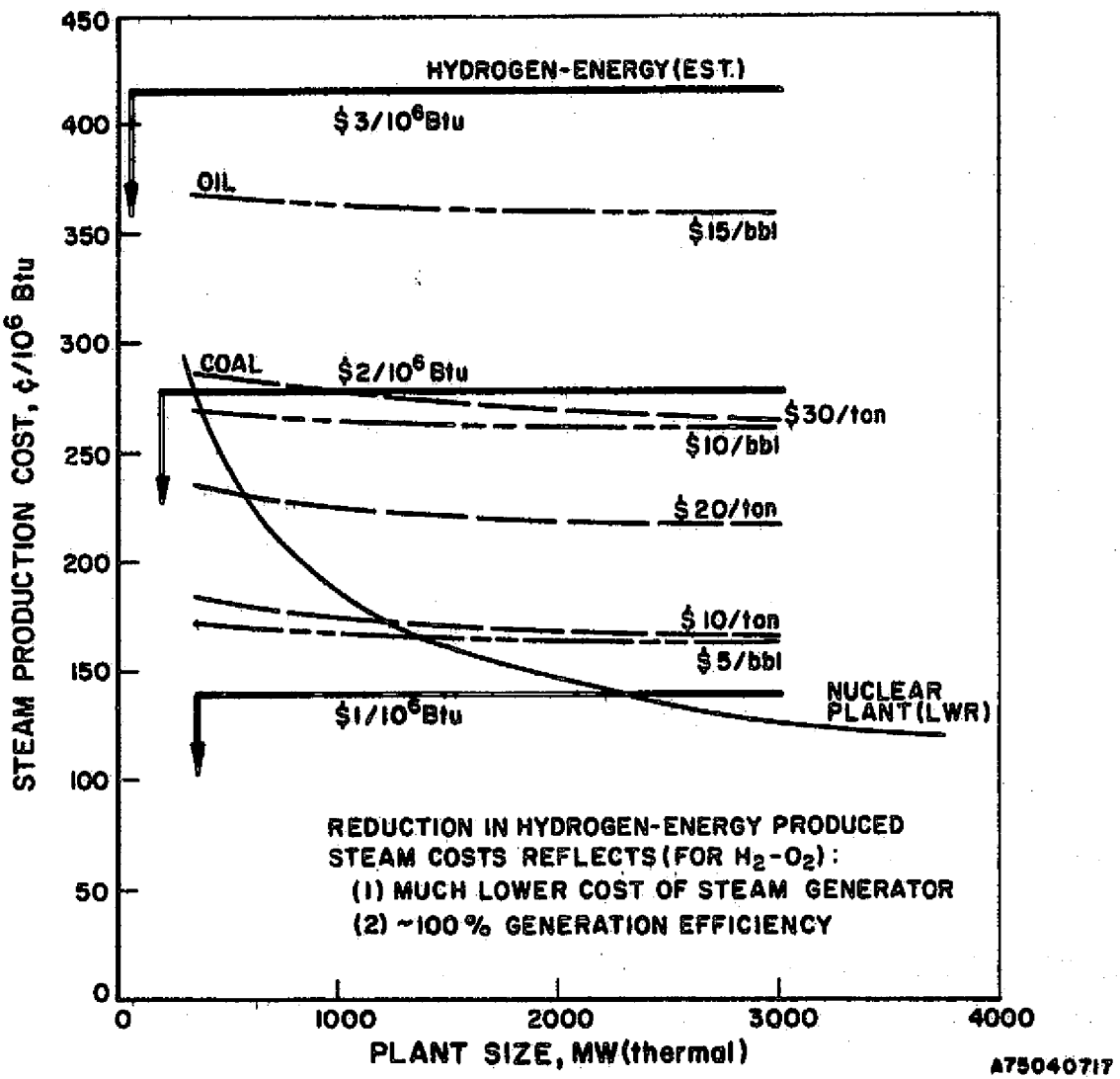

Figure 12-13. COMPARATIVE COSTS OF STEAM PRODUCTION
(Source: Womack & Laughon, AEC, 1974 – Hydrogen Estimates Added)

Hydrogenations and Oxo-Alcohol Production

Chemical syntheses of products other than ammonia and methanol consume only relatively small amounts of hydrogen. For example, oxo-alcohols are synthesized by reacting olefins with synthesis gas (carbon monoxide and hydrogen in a 1:1 molar ratio). A typical process reacts synthesis gas with propylene to form butylaldehyde, which is hydrogenated to alcohol:

$$C_3H_6 + CO + H_2 \rightarrow C_4H_8O$$
$$C_4H_8O + H_2 \rightarrow C_4H_9OH$$

Oxo-alcohols are used as plasticizers, especially in the production of vinyl resins. World capacity, which is growing at 15% annually, is currently 2.5 million tons/yr. Using the above reactions as a model, the world requirement for hydrogen to produce this quantity of oxo-alcohols would be about 25 billion SCF/yr.

Other processes that use hydrogen are the hydrogenation of benzene to cyclohexane (an intermediate in the production of nylon) and the hydrodealkylation of branched aromatics to obtain benzene, an important basic petrochemical.

Other Industrial Uses of Hydrogen

General

Hydrogen is also used in a large number of small-use sectors in industry, including –

- Float-glass production and glass cutting
- Semiconductor production
- Electrical-generator cooling
- Hydrogenation of edible organic oils and inedible tallow and grease.

These applications for "distributable hydrogen" are included in the special list of hydrogen applications by Standard Industrial Classifications (SIC), Appendix A-2.

Hydrogenation of Fats and Oils

In the nonchemical hydrogen category, the largest use of hydrogen is for the hydrogenation of fats and oils. Both edible and inedible oils are hydrogenated and are used in various products, such as baking and frying fats,

margarine, soap, paint, and varnish (drying oil). An order-of-magnitude estimate, derived from very limited survey data, is that this use consumes less than 10 billion SCF of hydrogen annually, based on a consumption of 15 billion pounds of fats and oils in 1973 [19] at a usage rate of 0.6 SCF of hydrogen per pound of product.

If economically tenable, fats and oils processes could readily use an outside stream of hydrogen. First, the small consumption per plant (from 0.5 to 2.0 million SCF/day) makes onsite steam reforming expensive. Second, pure hydrogen is required. Third, unlike other uses, these do not require other industrial gases, such as nitrogen or carbon monoxide. Fourth, hydrogenation is carried out at ambient temperature and at low pressures, so the gas could be used directly without heating or being greatly compressed.

References Cited in This Section

1. Aacund, L. R., "Refining Capacity Registers Largest Nickel and Dime Jump in History," Oil Gas J. 72, 76-79 (1974) April 1.

2. Barnham, T. F., U.S. Steel Corp., letter of February 24, 1974.

3. Biederman, N. P. and Darrow, K. G., Jr., "Utilization of Off-Peak Power to Produce Industrial Hydrogen," IGT Prelim. Rep. EPRI Project RP 320-1. Chicago, February 15, 1975.

4. Blanco, E. R. et al., "Ammonia Costs and Electricity," Chem. Eng. Prog. 63, No. 4, 46-50 (1967) April.

5. Blickwede, D. J. and Barnhart, T. F., "The Use of Nuclear Energy in Steelmaking — Prospects and Plans." Paper presented at the First Topical Meeting on Nuclear Process Heat, Los Alamos, N.M., October 1974.

6. Cantrell, A., Ed., "Annual Refining Survey," Oil Gas J. 72, 76-79 (1974) April.

7. Dyck, W. J., MacMullan, R. J. and Stotler, H. H., "Economics of Primary Iron and Steel Production in the West Coast From Local Iron Ores Via the 'H-Iron' Direct-Reduction Process," Can. Min. Metall. Bull. 56, 888-94 (1963) December.

8. Gregory, D. P., Anderson, P. J., Dufour, R. J., Elkins, R. H., Escher, W.J.D., Foster, R. B., Long, G. M., Wurm, J. and Yie, G. G., A Hydrogen-Energy System, Am. Gas Assoc. Cat. No. L21173. Arlington, Va.: American Gas Association, 1972.

9. Grimes, P. G., "Energy Depot Fuel Production and Utilization," Soc. Automot. Eng. Pub. SP-263, 1964.

10. Hedley, B., Powers, W. and Stobaugh, R. B., "Methanol: How, Where, Who – Future, Manufacture," Hydrocarbon Process. 49, 97-101 (1970) June.

11. Hedley, B., Powers, W. and Stobaugh, R. B., "Methanol: How, Where, Who – Future, Economics," Hydrocarbon Process. 49, 275-80 (1970) September.

12. Iammartino, N. R., "Direct Reduction Roundup," Chem. Eng. 81, 56-57 (1974) August 19.

13. Leppert, J. P., Factory Mutual Engineering, letter of July 14, 1973.

14. Linke, S., Ed., Proc. First Int. Symp. Workshop Hydrogen Econ. New York, 1975.

15. Los Alamos Scientific Laboratory, Proc. First Natl. Topical Conf. Nuclear Process Heat. Los Alamos, N.M., 1974.

16. Rollinger, B., "Steel Via Direct Reduction," Iron Steel Manuf., 10-16 (1975) January.

17. Stelzoff, S. and Pan, L. C., Synthetic Ammonia. New York: Chemical Construction Corp., n.d.

18. U.S. Bureau of Mines, "Hydrogen Commodity Statement – 1972," unpublished. Washington, D.C., 1973.

19. U.S. Department of Commerce, "Fats and Oils 1973," Curr. Ind. Rep. Ser. M20K(73)-13. Washington, D.C.: Bureau of the Census, 1974.

20. "Worldwide Direct Reduction Roundup," Iron Steel Manuf., 17 (1975) January.

21. Yarway Corp., Yarway Steam Conservation. Blue Bell, Pa., n.d.

13. RESIDENTIAL USE OF HYDROGEN – M. I. Scott, J. C. Gillis, and P. A. Ketels

The use of hydrogen as a residential fuel can be justified if hydrogen gas can be produced, delivered to, and utilized by residential customers more economically than can other energy forms. Hydrogen is thus a potential alternative to natural gas, oil, or electricity. The substitution of hydrogen for natural gas or oil would come about only if the prices or availability of these fuels dictated the change.

It should be noted that total conversion to hydrogen-energy utilization is not being advocated here. It is anticipated that a combination of energy forms will continue to be consumed – i. e., fuel gas and electricity. Some applications, such as lighting requirements and electric motors, are best served by electricity. However, eventually it may be beneficial to convert applications that currently consume fossil fuel (primarily natural gas) to hydrogen consumption because a distribution network already exists that has utilization equipment potentially capable of using hydrogen as a fuel after some modification.

Residential Energy-Use Patterns

Assessed in this report section is the feasibility of using hydrogen to suppl a substantial portion of the energy requirements for a single-family dwelling unit. This assessment of residential hydrogen utilization is based on the schematic diagram presented in Figure 13-1. It is made from the point at which energy enters the residential unit and will not be concerned with the factors effecting energy production, transmission, and distribution because these are accounted for in other parts of the report. As seen in Figure 13-1, we are concerned with both the present consumer of energy and the new customer. The present energy user already owns appliances and is faced with the probability of converting these appliances from present energy forms to new ones as the conventional fossil-fuel forms of energy are depleted. The decision to convert will be based on such factors as the age of a particular appliance, the cost of conversion, and the cost of alternative energy supplies.

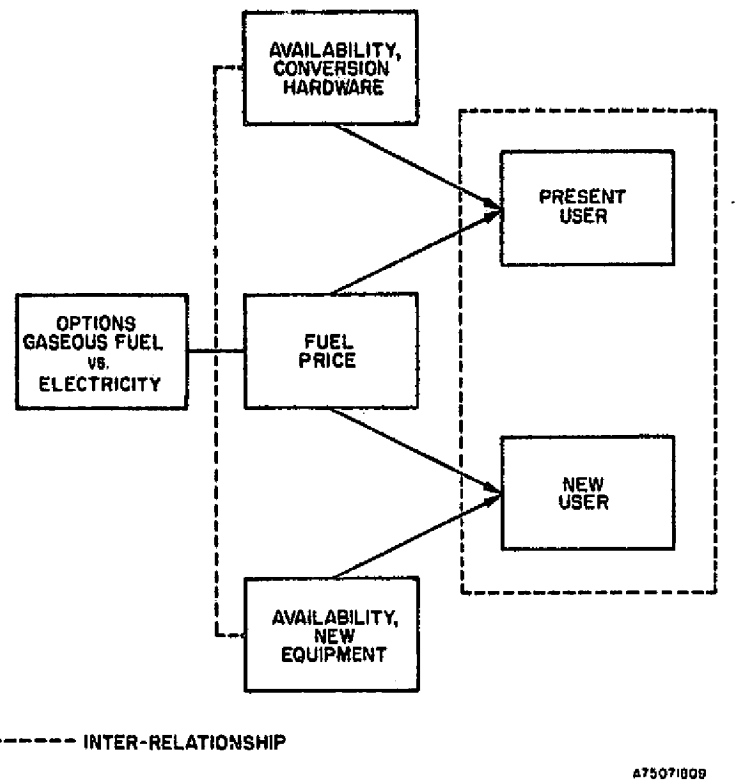

Figure 13-1. GASEOUS FUEL VERSUS ELECTRICITY

The new energy user does not currently own any appliances, but instead has to decide which to buy. The purchase decision is likely to be based on the cost and type of energy available to him and on the initial cost of the equipment. One exception to this is the availability of solar heating. It is assumed that such systems will be available within the near-term time frame; however, the cost of such a system is expected to be high, while the related energy or fuel cost will be zero (except for possible standby equipment). Should the new consumer choose some form of ready-built housing, the decision as to a specific configuration of appliances will already have been made for him.

Residential-Unit Characteristics

A prerequisite to a discussion of energy utilization in the residential market is knowledge of the quantities of various energy forms consumed for such purposes as space heating, cooling, cooking, water heating, clothes washing and drying, and lighting. For purposes of discussion and later comparison, a specific dwelling-unit type was chosen for use in quantifying residential energy consumption.[14] The consumption is not to be considered as representative of patterns across the United States, but merely serves as an example. This configuration, for a typical, single-family dwelling unit in the Northeastern United States, was developed by the Bureau of Census from data collected on housing construction techniques within that region. Table 13-1 is the resulting list of housing parameters. It can be seen that the unit outlined is dependent upon both natural gas and electricity as energy sources. Annual energy consumption within the above residence is shown, by application, in Table 13-2. The energy consumed is predicated on installation of the most modern appliances found in a newly constructed home.

Data on residential-appliance gas consumption are available from a number of sources. In this discussion we have chosen to use some information made available by a series of tests performed by Northern Natural Gas Co. of Omaha, Nebraska.[15] These data were selected because they are presented as a function of water temperatures for the ease of water-heating consumption. This method of data presentation makes the data useful and readily convertible to other geographic regions. The test data are actual measurements made in residential customers' homes through the use of specially installed meters that were monitored over a period of time.

It can be seen in Table 13-2 that space and water heating are the major energy-consuming applications within the given residential situation. It should also be noted that the quantity of electricity consumed within a residence can vary by a factor of 2 or more for a specified floor area. This variance in consumption can be primarily attributed to assorted living patterns, human factors, and the number and type of appliances within a particular situation.

Table 13-1. HOUSING PARAMETERS*

House Floor Area	1500 sq ft (finished)
House Style	Two story
House Construction	Wood frame
Exterior-Wall Construction	
Surface	Wood Shiplap
Sheathing	1/2-inch insulation board
Insulation	R-7 batting
Inside	1/2-inch dry wall
Ceiling Insulation	5 inches blown-in
Basement Type	Full (unfinished)
Attic	Ventilated, unheated
Window Area	12% of floor area
Window Type	Al casement
Storm Windows	None
Door Area (3 Doors)	60 sq ft
Door Type	Wood panel with 0.5 sq ft of glass pane
Storm-Door Area	40 sq ft
Patio Door	40 sq ft (single pane)
Window Covering	70% draped
	20% shaded
	10% open
	No awnings
External Landscaping	No shading effect
Direction House Faces	North
External Colors	White roof and walls
Roof Construction	Asphalt shingle
Heating System	Forced hot air, natural gas
Cooling System	Central, electric
Garage (Enclosed)	Attached, slab, unheated
Residents	Two adults, two children
Location	Northeastern region of U.S.

*In addition to the above housing characteristics, external weather conditions must be defined.

Table 13-2. ANNUAL ENERGY CONSUMPTION IN RESIDENTIAL UNIT, NORTHEAST REGION

Natural Gas Load	Energy Consumed, 10^6 Btu	% of Total Consumption
Space Heating	132.0	64.8
Water Heating	27.0	13.3
Cooking	6.4	3.1
Clothes Drying	3.4	1.7
Subtotal	168.8	82.9
Electric Load		
Central Air Conditioning	12.5	6.1
Lighting	6.8	3.3
Refrigerator-Freezer	6.2	3.1
Clothes Washer	0.3	0.2
Color TV	1.7	0.8
Furnace Fan	1.3	0.6
Dishwasher	1.2	0.6
Iron	0.5	0.2
Coffee Maker	0.4	0.2
Miscellaneous	4.1	2.0
Subtotal	35.0	17.1
Total	203.8	100.0

Space Heating

Space heating is the single largest energy-consuming application within the example dwelling unit. As shown in Table 13-2, it accounts for 64.8% of the total energy consumed.

The estimated annual gas consumption for space heating in single-family dwellings, by size, is presented in Figure 13-2. Data are presented for house sizes ranging from 800 to 2000 sq ft of floor area and for annual degree days* ranging from 5000 to 10,000. The estimated annual gas composition can be seen to vary from 100,000 to 280,000 SCF. The estimated peak-day requirements by house size at an average daily outdoor temperature of 0° F are presented in Table 13-3. These data are useful in illustrating the changes in consumption levels for dwelling units of various sizes.

*Degree-day heating: A measure of the coldness of the weather experienced based on the extent to which the daily mean temperature falls below a reference temperature, usually 65° F. For example, on a day when the mean outdoor dry-bulb temperature is 35° F, there would be 30 degree days experienced. A daily mean temperature usually represents the sum of the high and low readings for the day divided by two.

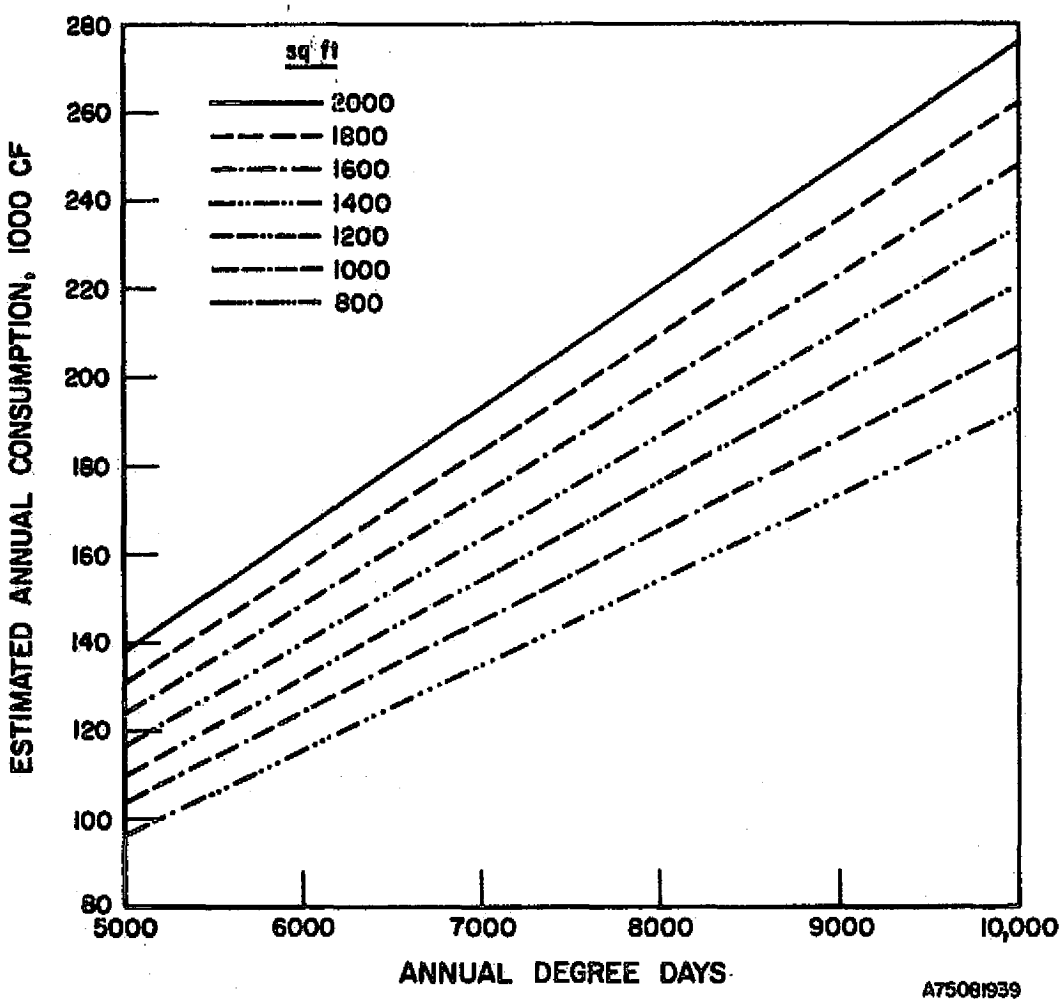

Figure 13-2. ESTIMATED ANNUAL CONSUMPTION BY DWELLING-UNIT SIZE

Table 13-3. ESTIMATED PEAK-DAY NATURAL GAS REQUIREMENTS BY HOUSE SIZE AT AN AVERAGE DAILY TEMPERATUE OF 0° F

House Size, sq ft	Peak Day, SCF
800	1302
1000	1398
1200	1494
1400	1590
1600	1685
1800	1781
2000	1877

The standing pilot flames associated with present residential space-heating equipment consume about 20 to 35 SCF of natural gas/day. At the average rate of 27 SCF/day, the heating unit will have an annual pilot-light load of approximately 10,000 SCF if the pilot burns throughout the entire year. The pilot-light load is included in the quantity of annual energy consumed listed above.

Water Heating

The annual quantity of energy required for water heating is more dependent upon the number of occupants in a home than on the number of degree days. The estimated water-heating load is presented in Table 13-2 and is equivalent to about 13.3% of the total energy consumption. It can be seen in Table 13-4 that annual energy consumption varies directly with the number of family members. For the family of four presented in the example dwelling unit, the energy consumed on an annual basis is about 41,000 SCF.

Table 13-4. ANNUAL WATER-HEATING LOAD, BY FAMILY SIZE

Occupants, No.	Estimated Load, SCF
1	32,820
2	35,660
3	38,500
4	41,336
5	44,176
6	47,016
7	49,855
8	59,691

There is a seasonal variation in the amount of energy required that is related to the temperature of the incoming water. Because the city water supply is warmer in the summer than in the winter, less heat is required to bring it to the desired thermostatically controlled temperature. This variation is shown in Figure 13-3. It can be seen that water-heating loads peak in the winter season at a value approximately 30% above the summer level.

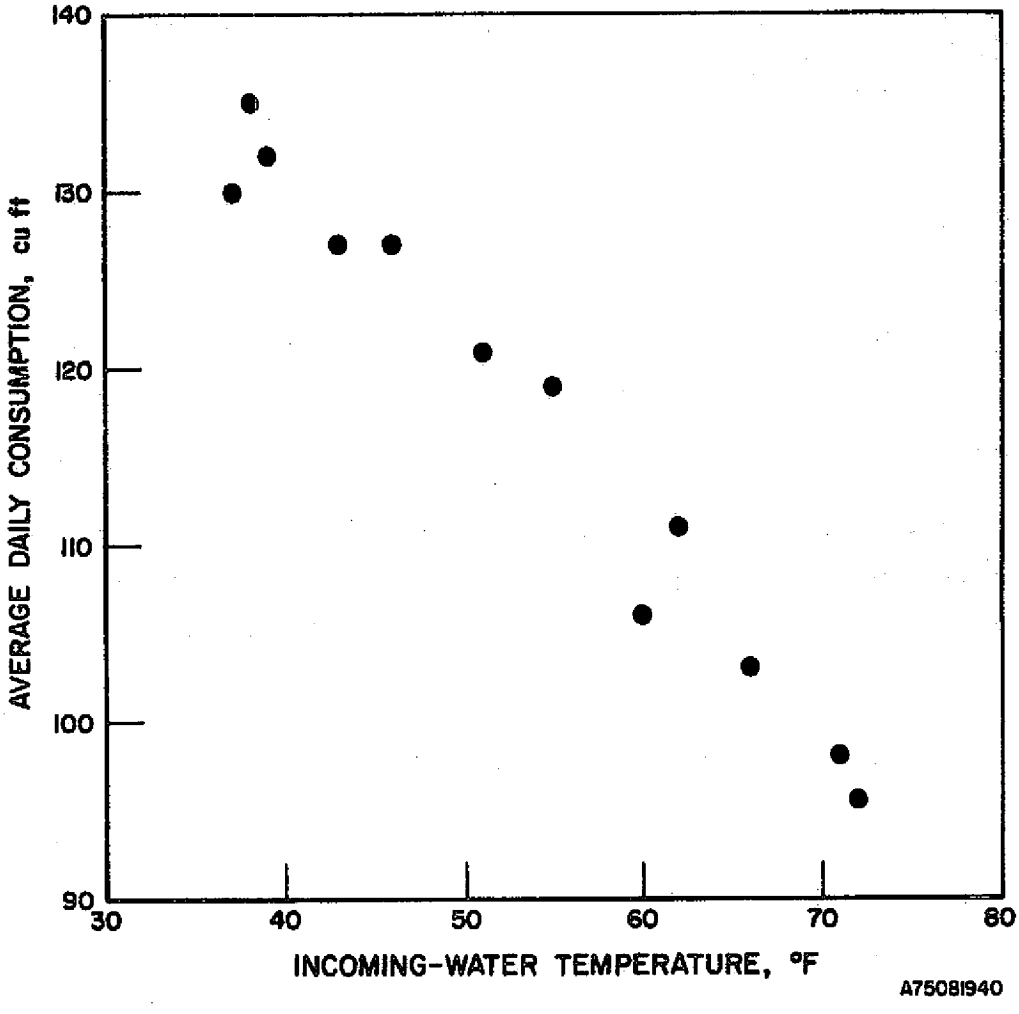

Figure 13-3. COMPARISON OF AVERAGE MONTHLY WATER TEMPERATURE AND AVERAGE DAILY WATER-HEATER CONSUMPTION, BY MONTH

The pilot-light load for water heating with natural gas is estimated at about 17 SCF/day, or 6200 SCF/yr. (These loads are included in the estimates presented in Table 13-2.) The range is 24 SCF/day, with the majority of the units consuming between 15 and 20 SCF/day.

Cooking

The natural gas requirement for cooking in our example dwelling unit is about 6.4 million Btu/yr. This is equivalent to 3.1% of the total energy consumed, as shown in Table 13-2. The pilot-light consumption is a major

factor in cooking ranges and accounts for about 60% of the total amount, or 2.4 million Btu. The magnitude of the annual gas load for use in cooking is difficult to relate to family size because of existing variations in individual cooking habits.

The peak-day cooking load occurs, as might be expected, on either Christmas or Thanksgiving Day. Some heavy cooking loads also occur during July and August and can be attributed to the canning season.

Clothes Drying

The estimated annual natural gas requirement for clothes drying, as in the case of water heating, is dependent upon the number of occupants in the dwelling. As shown in Table 13-2, the amount of energy consumed in clothes drying is about 3.4 million Btu, or 1.7% of the total energy consumption. A tabulation of estimated annual gas loads for clothes drying, based on the number of occupants, is shown in Table 13-5.

Table 13-5. ESTIMATED ANNUAL DRYER LOAD, BY FAMILY SIZE

Number of Occupants	Estimated Load, SCF
2	2321
3	3391
4	4464
5	5533
6	6606
7	7680
8	8740

The estimated loads shown in Table 13-5 do not include pilot-light consumption because gas pilot flames are used only a small number of gas dryers currently in use. Generally, electric ignition systems are installed on the more expensive gas dryers. For dryers without electric ignition of the dryer flame, an annual load of approximately 3000 SCF should be added to the estimates listed in Table 13-5. It should be noted that in the case of two occupants per dwelling unit, the pilot light consumes more natural gas over the period of a year than does the operating load.

Electricity Consumption

The electric load in the example dwelling unit accounts for 17.1% of the total annual energy consumption. As shown in Table 13-2, this is equivalent to 35 million Btu, or 10,255 kWhr. As in the case of cooking, the consumption of electricity is dependent upon many variables that cannot be

measured as accurately as degree days, nor can it be based simply on the number of occupants.

At present, the amount of electricity consumed within a residence can vary by a factor of 2 for any given floor area. The increase in the use of electricity within a residential unit can be illustrated by the history of New York State usage over 10 years (from 1960 to 1970). (See Figure 13-4.) The annual electrical use per customer has almost doubled. This trend has been created by the addition of appliances that are principally conveniences. The quantity of electricity consumed by various appliances on an annual basis is shown in Table 13-6.

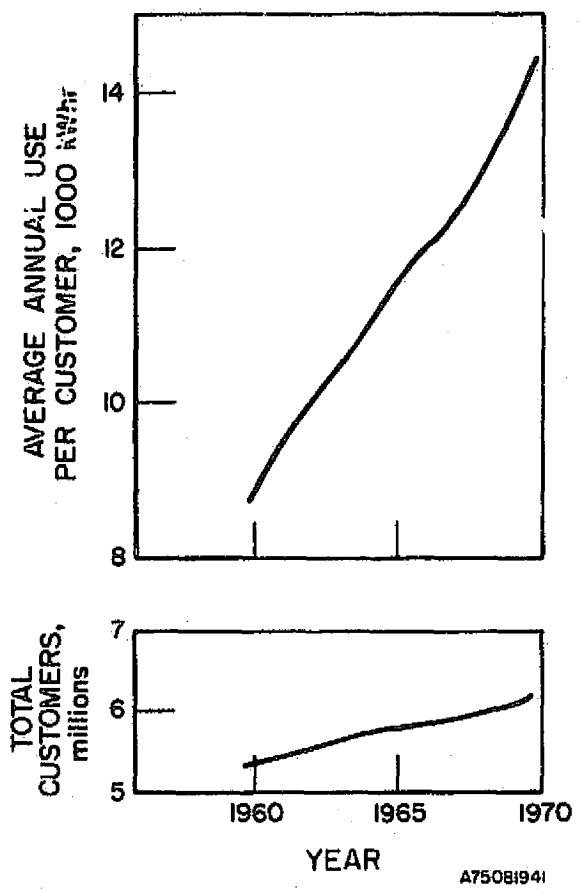

Figure 13-4. HISTORICAL ELECTRICITY GROWTH, NEW YORK STATE

The Use of Hydrogen in Domestic Appliances

If hydrogen is to replace natural gas in residential appliances, the behavior of hydrogen in burners designed to combust natural gas must be explored.

Table 13-6. ENERGY CONSUMPTION BY ELECTRIC APPLIANCES (Source: Edison Electric Institute, Marketing Division, 1969)

Appliance	Average Wattage Rating	Estimated Annual Consumption, kWhr
Air Conditioner* (Window)	1,566	1,389
Bed Covering*	177	147
Broiler	1,436	100
Carving Knife	92	8
Clock	2	17
Clothes Dryer	4,856	993
Coffee Maker	894	106
Cooker (Egg)	510	14
Deep-Fat Fryer	1,448	83
Dehumidifier*	257	377
Dishwasher	1,201	363
Fan (Attic)	370	291
Fan (Circulating)	88	43
Fan (Furnace)*	292	394
Fan (Rollabout)	171	138
Fan (Window)*	190	165
Floor Polisher	305	15
Food Blender	386	15
Food Freezer (15 cu ft)	341	1,195
Food Freezer (Frostless, 15 cu ft)	440	1,761
Food Mixer	127	13
Food Waste Disposer	445	30
Frying Pan	1,196	186
Germicidal Lamp	20	145
Grill (Sandwich)	1,161	33
Hair Dryer	381	14
Heat Lamp (Infrared)	250	13
Heater (Radiant)	1,322	176
Heating Pad	65	10
Hot Plate	1,257	90
Humidifier	117	163
Iron (Hand)	1,008	144
Iron (Mangle)	1,465	165
Oil Burner or Stoker	266	410
Radio	71	86
Radio-Phonograph	109	109
Range	12,207	1,175
Refrigerator (12 cu ft)	241	725
Refrigerator (Frostless, 12 cu ft)	321	1,217
Refrigerator-Freezer (14 cu ft)	326	1,137
Refrigerator-Freezer (Frostless, 14 cu ft)	615	1,829
Roaster	1,333	205
Sewing Machine	75	11
Shaver	14	18
Sun Lamp	279	16
Television (B&W)	237	362
Television (Color)	332	502
Toaster	1,146	39
Tooth Brush	7	5
Vacuum Cleaner	630	46
Vibrator	40	2
Waffle Iron	1,116	22
Washing Machine (Automatic)	512	103
Washing Machine (Nonautomatic)	286	76
Water Heater†	2,475	4,219
Water Pump	460	231

* Estimated for season (6 months) of peak use.

† Based on special water heating rate.

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The following discussion is intended to show why hydrogen cannot be directly substituted into residential appliances and what burner modifications would be necessary before hydrogen could be used as a fuel. It should be kept in mind that similar equipment modifications were necessary when natural gas was substituted for manufactured gas.

Hydrogen has a number of combustion properties that can be beneficially exploited with burners that operate through the action of a catalyst (i.e., catalytic burners) rather than through the action of a flame (i.e., atmospheric burners). The experimental work performed to date on such burners will also be described.

Conversion of Existing Appliances

Atmospheric Burners

The burners built into domestic gas appliances are designed to burn fuel from a low-pressure (from 3 to 16 inches water column) gas source, and so they are known as "atmospheric burners." These burners operate on the same principles as a Bunsen burner.

A Bunsen burner consists of a straight, smooth metal tube with a gas-metering orifice at the lower end. Ambient air enters the tube through adjustable openings around the gas orifice and is transported (entrained) by the high-velocity gas stream (jet). The air-gas mixture is ignited as it emerges from the upper end of the tube (the burner port). The air supplied through the burner openings near the metering orifice, before combustion, is primary air. Ambient air mixed after ignition is secondary air. Figure 13-5 shows the basic construction and nomenclature of an atmospheric gas burner.

During operation, gas issues at a high velocity from the gas orifice (which also meters the gas flow into the burner), creating a vacuum or lowered pressure, which allows the primary air to enter and mix with the gas. While continuing to mix, the air-gas mixture moves down the tube and into the burner head. The mixture passes through the ports and is ignited. The amount of primary air is described as a percent of the theoretical air required for complete combustion. For example, 9.56 CF of air is required to burn 1 CF of methane (CH_4):

$$CH_4 + 2O_2 + 7.56N_2 \rightarrow CO_2 + 7.56N_2 + \text{heat} \qquad (13\text{-}1)$$

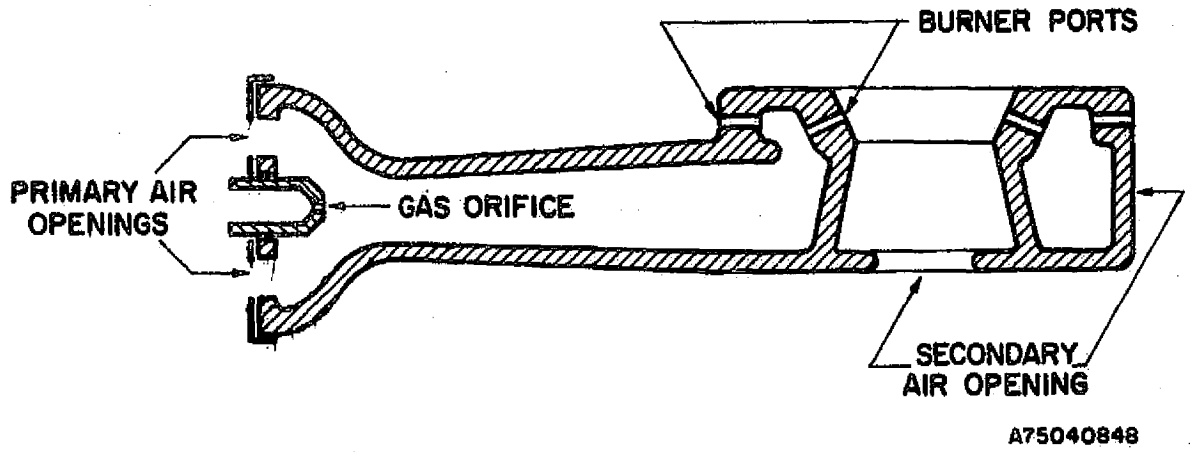

Figure 13-5. PRINCIPAL PARTS OF A TYPICAL ATMOSPHERIC BURNER

Therefore, a 65% primary air mixture would have 6.214 CF of air mixed with 1 CF of methane. The balance of the air required to complete combustion – i.e., 3.346 CF – would then be secondary air. Figure 13-6 shows flame geometry as a function of percent of primary air and natural gas.

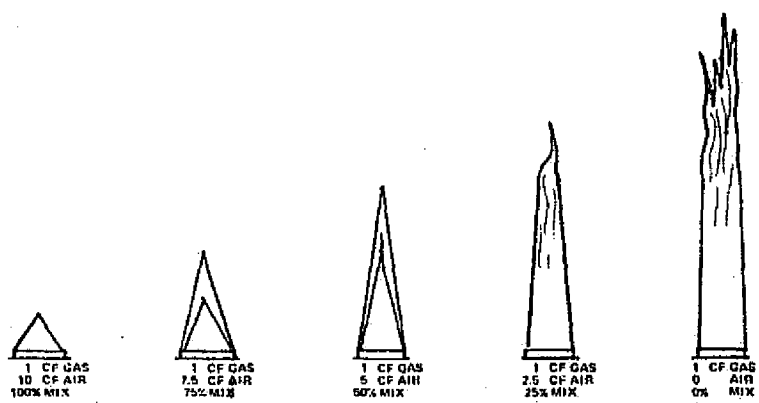

Figure 13-6. FLAME GEOMETRY VERSUS PERCENT AERATION[15]

For efficient operation, atmospheric burners must be able to perform under a wide variety of field conditions and must meet the following basic requirements[5]:

- Controllability over a wide range of turn down without danger of flash-back or flame-out
- Uniform distribution of heat, including uniform flame height and good flame distribution over the area being heated
- Complete combustion – i.e., no formation of carbon (soot) or carbon monoxide (CO)*
- No lifting of the flame away from the ports
- Ready ignition – i.e., the flame traveling rapidly and without difficulty from port to port over the entire burner
- Quiet operation upon ignition, during burning, and upon extinction.

Contemporary atmospheric burners are capable of efficient operation over a wide range of input pressures. Range burners, for example, will operate at input pressures ±50% of the normal pressure of 7 inches water column (0.253 lb/sq in.).[2] Atmospheric burners can also be designed to burn any of a variety of fuel gases, some properties of which are shown in Table 13-7.

Table 13-7. GAS MIXTURES USED WITH CONTEMPORARY ATMOSPHERIC-TYPE RESIDENTIAL BURNERS

Type of Fuel Gas	High (Gross) Heating Value, Btu/cu ft	Specific Gravity (Air = 1.0)
Natural	1075	0.65
Manufactured	535	0.38
Mixed	800	0.50
Butane	3175	2.00
Propane	2500	1.53
Butane-Air	525	1.16
Butane-Air	1400	1.42

* It should be noted that during start-up carbon monoxide may be formed if the flame is quenched by a cold target (e.g., water in a water heater).

Tables 13-8 and 13-9 give the physical and operating descriptions of the representative atmospheric gas burners used on residential appliances and a calibration-type Bunsen burner shown in Figures 13-7 and 13-8, respectively.

The following discussion compares the performance of unmodified burners on natural gas and on hydrogen and shows what modifications should be made during conversion of appliances from natural gas to hydrogen.

Fuel Flow Rate

The gross (high) heating value of a typical natural gas is approximately 1060 Btu/SCF, but the gross heating value of hydrogen is only 325 Btu/SCF. Thus for a burner operating on hydrogen to deliver the same amount of heat as one operating on natural gas, per unit time, it will have to pass 3.26 times as much fuel (by volume). Superficially this would seem to preclude the use of hydrogen in existing appliances without extensive modification. However, the flow of compressible fluids through nozzles (or metering orifices) is governed by the Bernoulli theorem, which can be expressed as —

$$q = YCA(h_L/\rho)^{0.5} \qquad (13\text{-}2)$$

where —

q = flow rate through the nozzle or orifice, CF/hr

Y = expansion factor (function of specific heat ratio, ratio of orifice or throat diameter to inlet diameter, and ratio of downstream to upstream absolute pressures)

C = coefficient of discharge

A = area of orifice, sq in.

h_L = the measured differential static head or pressure across the burner port, in. wc

ρ = specific gravity of gas (air = 1).

If the value of the term YCA is assumed constant for the two gases, natural gas and hydrogen, and the pressure (h_L) is held constant for the same orifice, the relative flow rates would be —

$$q(H_2) = q(\text{nat. gas})[(0.599/0.0696)]^{0.5} \qquad (13\text{-}3)$$

$$q(H_2) = q(\text{nat. gas})(2.93)$$

Table 13-8. IDENTIFICATION AND DESCRIPTION OF THE BURNERS IN FIGURE 13-7

Item No.	Input Rating, Btu/hr	Total No. Ports	Total Port Area, sq in.	Burner Construction Material	Appliance
1	6,600	48	0.33	Cast iron	Range
2	12,800	64	0.64	Cast iron	Laundry boiler
3	45,000	34	0.63	Cast iron	Water heater
4	9,000	52	0.28	Aluminum	Range
5	9,000	70	0.23	Aluminum	Range
6	12,000	72	0.39	Aluminum	Range
7	5,000	1	0.15	Aluminum	--

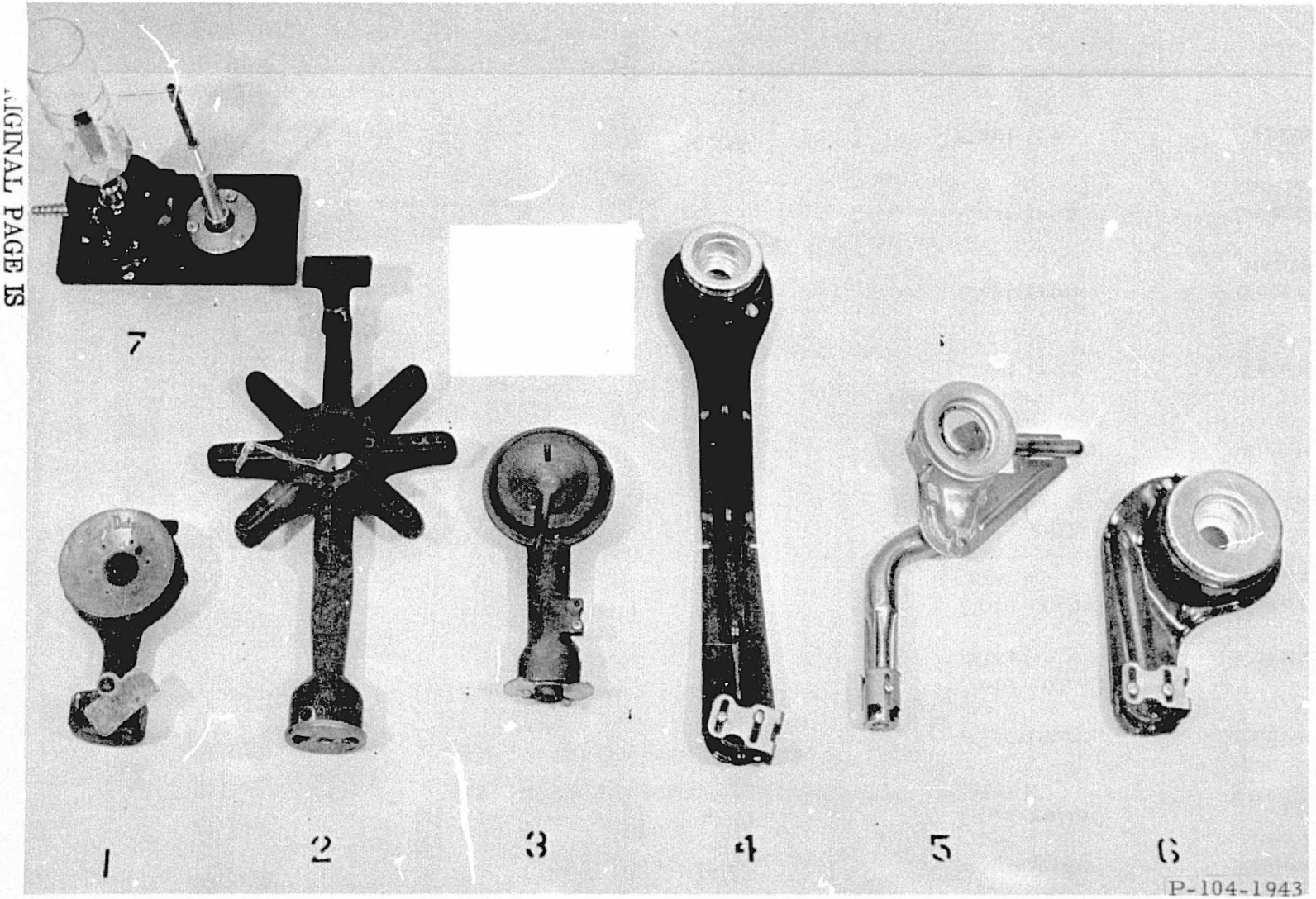

Figure 13-7. REPRESENTATIVE ATMOSPHERIC GAS APPLIANCE BURNERS (DOMESTIC) AND A CALIBRATION BUNSEN BURNER

Table 13-9. IDENTIFICATION AND DESCRIPTION OF THE BURNERS IN FIGURE 13-8

Item No.	Input Rating, Btu/hr	Total No. Ports	Total Port Area, sq in.	Burner Construction Material	Appliance
1	5,000	1	0.15	Aluminum	--
2	9,000	48	0.23	Aluminum	Range
3	30,000	55	1.79	Cold rolled steel	Furnace
4	9,000	69	0.26	Aluminum	Range
5	12,000	72	3.02	Cold rolled steel	Furnace
6	27,500	1	0.91	Cold rolled steel	Water heater
7*	40,000	20	0.02	Cold rolled steel	Water heater
8	75,500	42	1.13	Cold rolled steel	Water heater
9	48,000	34	0.63	Cast iron	Water heater
10	6,600	48	0.33	Cast iron	Water heater
11	12,800	64	0.64	Cast Iron	Laundry boiler
12	15,000	105	0.76	Cast iron	Broiler

* Uses secondary air only.

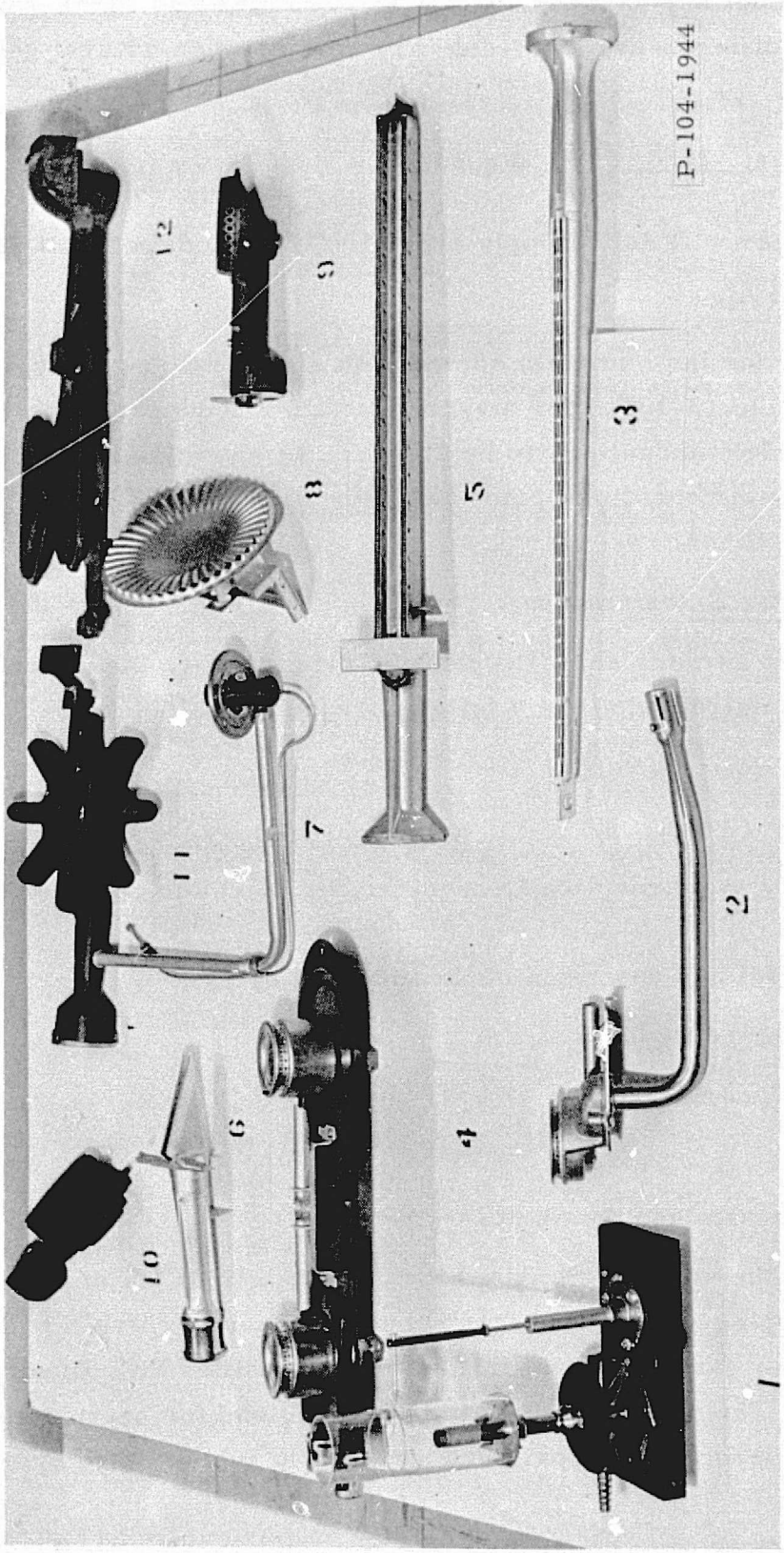

Figure 13-8. CONTEMPORARY GAS APPLIANCE BURNERS (DOMESTIC) WITH A VARIETY OF PORT CONSTRUCTIONS AND A CALIBRATION BUNSEN BURNER

Thus the burner, without any changes, will pass 2.93 times as much hydrogen as natural gas. The difference in heat-delivery rate between natural gas and hydrogen is then –

$$\frac{(325/1060)}{(1/2.93)} = 0.898 \qquad (13\text{-}4)$$

and the hydrogen burner will deliver only about 10% less heat per unit time.

Air/Fuel Ratio

The air/fuel ratio for the complete combustion of natural gas is approximately 10:1. (See Table 13-10.) The air/fuel ratio for hydrogen is calculated, based on stoichiometric combustion, to be 2.38:1. As shown in Figure 13-6, the amount of primary air entrained prior to combustion greatly effects the characteristics of the flame.

Primary-Air Entrainment

Tests on numerous burners show that, for a given burner, the percentage of primary air that is entrained closely follows the empirical equation[5] –

$$IP = K[(Pd)^{0.25}/(H)^{0.5}]/R^{0.5} \qquad (13\text{-}5)$$

where –

IP = entrained primary air theoretically required for complete combustion, percent

P = pressure of the fuel gas upstream of the entering orifice

d = specific gravity of the fuel gas

H = heating value of the fuel gas

R = energy input rate

K = experimentally determined constant.

Table 13-11 gives the values calculated for comparison of the ability of an assumed 10,000 Btu/hr-input rated atmospheric burner to entrain primary air using gases (natural gas and hydrogen) that have densities that differ by approximately 860%. The values of IP/K for hydrogen and for natural gas indicate that a higher percentage of primary air will be entrained by hydrogen than by natural gas.

Table 13-10. CHEMICAL ANALYSIS OF A HIGH-METHANE ADJUSTMENT GAS

Component	Chemical Formula	Cu Ft/ Cu Ft of Gas	Sp Gr X % Gas	High (Gross) Heating Value,[15] Btu	Air Required for Complete Combustion, cu ft
Methane	CH_4	0.9363	0.518	947.84	8.950
Ethane	C_2H_6	0.0358	0.037	63.49	0.597
Propane	C_3H_8	0.0102	0.016	25.74	0.248
Butane	C_4H_{10}	0.0040	0.008	13.06	0.124
Pentane	C_5H_{12}	0.0012	0.003	4.82	0.046
Hexane	C_6H_{14}	0.0008	0.002	3.81	0.040
Carbon Dioxide	CO_2	0.0070	0.011	--	--
Nitrogen	N_2	0.0047	0.004	--	--
Total		1.000	0.599	1058.76	10.005

Table 13-11. VALUES OF A 12,000 Btu/hr ATMOSPHERIC BURNER'S AIR INJECTING ABILITY FOR A HIGH-METHANE NATURAL GAS AND HYDROGEN

	Fuel Gas	
	Natural Gas	Hydrogen
P, in. wc	7.0	7.0
d (Air = 1)	0.6	0.07
H, Btu/SCF	1059	32.5
R, Btu/hr	10,000	10,000
$Pd^{0.15}$	1.43	0.837
$H^{0.5}$	32.54	18.03
$R^{0.5}$	100.0	100.0
$IP/K \times 10^5$	43.9	46.4

Table 13-12 gives the typical primary-air requirements for appliance burners operating on natural gas. If we assume the range-top burner is adjusted for natural gas (60% primary air) and we replace the natural gas with hydrogen, the primary aeration for the substitution would equal, by Equation 13-7, 85%.

Table 13-12. MINIMUM PRIMARY-AIR REQUIREMENTS FOR VARIOUS TYPES OF APPLIANCE BURNERS[3]

Type of Burner	Primary-Air Portion of the Total Theoretically Required Air, %
Range Top	55-60
Range Oven	35-40
Water Heater	35-40
Radiant-type Space Heater	65
Other Heating Appliances	As low as 35

Burning Velocity

The burning velocity of natural gas, using 100% of the theoretically required air, is about 1 ft/s.[3] The burning velocity of hydrogen, however, has been measured at 9.2 ft/s using only 57% of the theoretically required air. Because the hydrogen flame is so much faster than the methane flame, there may be the difficulty of flashback with hydrogen burners.

Flashback is the propagation of the flame front back through the burner ports and upstream to the metering orifice. The flame cannot travel through

the orifice because the gas upstream is pure fuel and cannot sustain combustion. However, if combustion takes place at the metering orifice instead of at the burner ports, the burner head may be severely damaged.

The tendency of a burner to flashback is indicated by the boundary velocity gradient of the burner port. The boundary velocity gradient can be derived from Poiseuille's Law (the basic equation for laminar flow in ducts), which is expressed as[14] –

$$\nu_g = k(R^2 - r^2) \qquad (13\text{-}6)$$

where –

ν_g = gas velocity

k = a constant

R = gas stream radius

r = distance from stream center

The value of the constant (k) can be determined by using volume flow per unit time – i.e., gas flow rate – and the tube radius (R):

$$k = 2V/\pi R^4 \qquad (13\text{-}7)$$

where V is the volumetric flow rate. Substituting the value of k into Equation 13-6, the gas velocity (ν) is calculated to be –

$$\nu_g = (2V/\pi R^4)(R^2 - r^2) \qquad (13\text{-}8)$$

The average value of the gas velocity ($\bar{\nu}_g$) is –

$$\bar{\nu}_g = 4V/3\pi R^2 \qquad (13\text{-}9)$$

Figure 13-9 shows the velocity profile of a gas stream from a burner port. Figure 13-10 shows the interplay between the gas velocity (ν_g) and the flame speed (ν_f).

Assuming that the inner cone* of a flame from a Bunsen burner is a right cone – that is, a true cone of revolution – and that the air-gas flow is laminar, by definition,[3] the flame velocity (ν_f) is the component of the average air-gas velocity (ν_g) in a direction perpendicular to the flame front, as shown in

* It is also assumed that within the inner cone there exists only an unburned gas mixture.

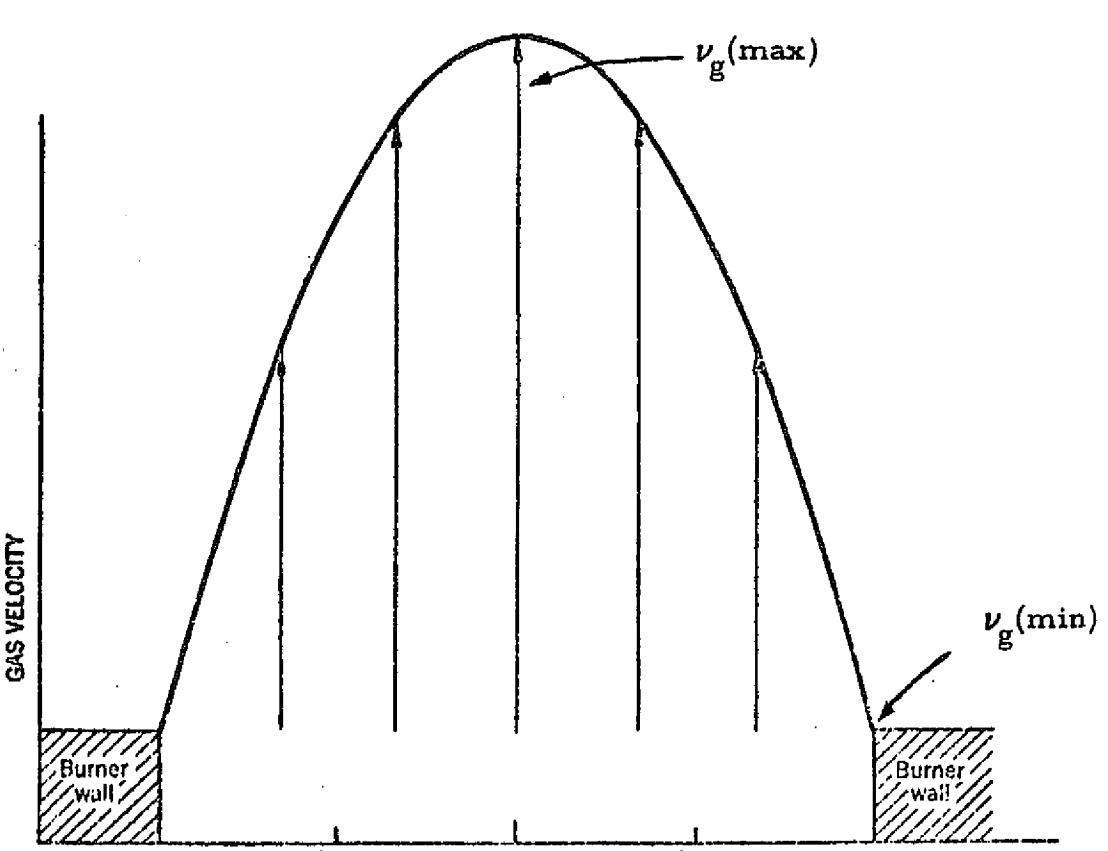

Figure 13-9. PARABOLIC VELOCITY PROFILE OF A STREAM AT A BURNER PORT[4]

Figure 13-10. MIXTURE VELOCITY VERSUS FLAME SPEED [10]

Figure 13-11. Therefore, from Figure 13-11 –

$$\nu_f = \bar{\nu}_g \sin \theta \qquad (13\text{-}10)$$

under stable conditions.

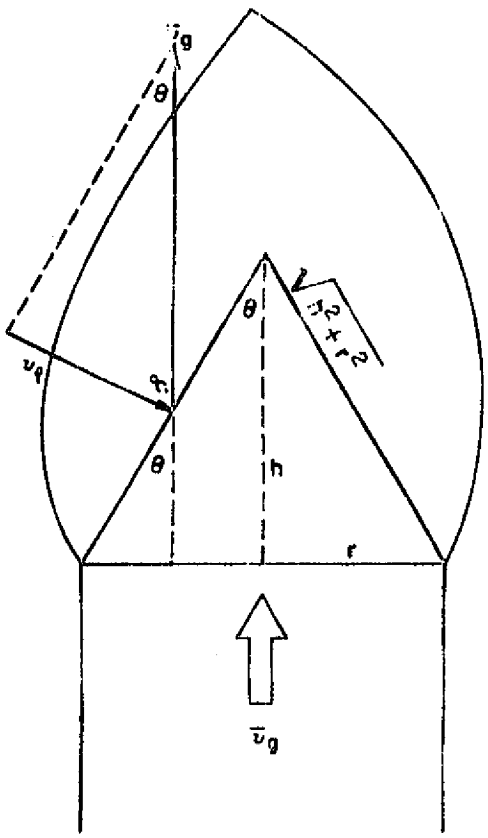

Figure 13-11. FLAME FROM A BUNSEN BURNER WITH A TRUE CONE-OF-REVOLUTION INNER CONE

If Equation 13-6 (Poiseuille's Law) is differentiated with respect to r, setting r equal to R, the boundary velocity gradient can be obtained:

$$\text{grad } \nu_b = 4V/\pi R^3 \qquad (13\text{-}11)$$

However, when the burner port diameter is so large that the air-gas velocity (ν_g) profile at the wave fringe may be considered linear, the air-gas velocity equation may be approximated by the equation –

$$\nu_g = \text{grad } \nu_b \cdot d \qquad (13\text{-}12)$$

where d is the distance from the stream boundary.

Thus the gas velocity at any d is proportional to the velocity gradient; and if a state is reached in which the gas velocity (ν_g) at some point becomes smaller than the burning velocity (ν_f), the combustion wave propagates back against the gas stream into the tube — that is, it flashes back. At limiting conditions for lifting flames (blowoff), grad ν_g becomes the critical boundary velocity gradient. At this value, the air-gas velocity (ν_g) exceeds the burning velocity (flame speed, ν_f), and blowoff occurs.

The results of the investigations by Grumer, Harris, and Rowe (of the U.S. Bureau of Mines),[8] concerning flashback, lift-off, and stability of methane-air and hydrogen-air mixtures, are shown in Figures 13-12 through 13-14. In general, a hydrogen flame can be leaner than a methane flame before blowoff will occur; however, the velocity gradient (ν_b) must be maintained at a higher level to prevent flashback. To prevent flashback, the values from Figures 13-12 through 13-14 indicate that at the critical boundary values for stoichiometric mixtures of hydrogen and air, the average gas velocity ($\bar{v}_g$) of hydrogen should be approximately 9 times greater than the average velocity of methane.

The experimental results shown in Figures 13-12 through 13-14 were obtained from measurements taken on single-port Bunsen burners and are not strictly applicable to multiport burners found in contemporary appliances. However, if Equation 13-11 is applied to a typical Bunsen burner (for example, burner No. 1 in Table 13-9), the boundary velocity gradient is found to be approximately 2000 (assuming 60% primary air stoichiometric). Figure 13-12 shows that the burner will then be operating in stable-flame range. If the same burner were operated on hydrogen (with no adjustments), the boundary velocity gradient, calculated by using the analysis of the air/fuel ratio, primary-air entrainment, and fuel flow rate shown above, would be about 2600 at a gas concentration of 1.18 times stoichiometric. Figure 13-14 shows that flashback would then occur. Again, it should be remembered that the flashback characteristics of real appliance burners cannot be accurately determined by analysis of single-port burners and that their tendency to flash back when operated on hydrogen must be determined experimentally.

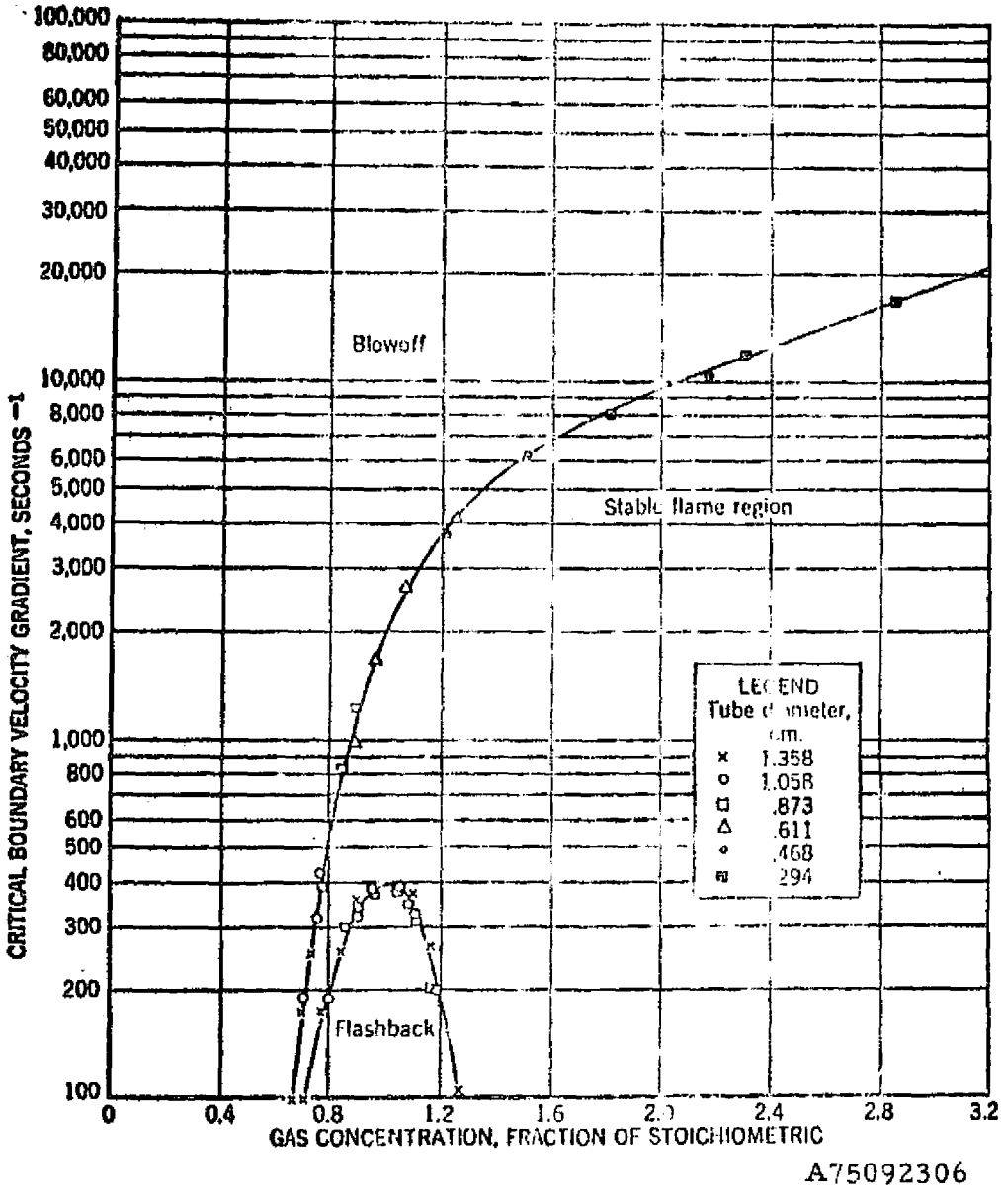

Figure 13-12. FLAME-STABILITY DIAGRAM FOR A FUEL CONTAINING 100% METHANE[8]

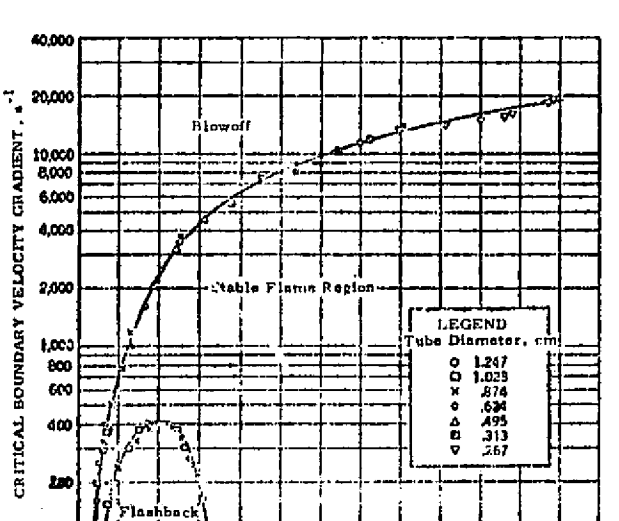

Figure 13-13. FLAME-STABILITY DIAGRAM FOR NATURAL GAS[5] (91.5% CH_4, 5.2% C_2H_6, 1.3% C_2H_8, 0.9% CO_2, 0.6% N_2, 0.2% C_3H_6, 0.2% C_4H_{10}, 0.1% C_4H_8)

One of the consequences of hydrogen's high flame speed is a change in the shape of the flame. A standard natural gas flame is a cone about 1/8 inch high; but with hydrogen, the flame will be much shorter. To show this, we assume a natural gas flame height of 3.17 mm and a port radius of 0.377 mm. From Equations 13-3 and 13-10 —

$$\nu_g(\text{nat. gas}) = 8.5 \text{ ft/s}$$
$$\nu_g(\text{hydrogen}) = (2.93)(8.5) \quad 24.9 \text{ ft/s} \qquad (13\text{-}13)$$

From Figure 13-11 —

$$h \text{ (inner cone flame height)} = r \cot \theta \qquad (13\text{-}14)$$

and, from our assumptions, r equals 0.377 mm. Therefore, for hydrogen h equals 0.948 mm. This indicates a decrease in height of approximately 70%. If, however, the velocity of the hydrogen is increased by a factor of 9 to stop flashback, h equals 3.11 mm; and the change in inner-cone flame height would be only 2%. If the flame height is to be maintained, the velocity

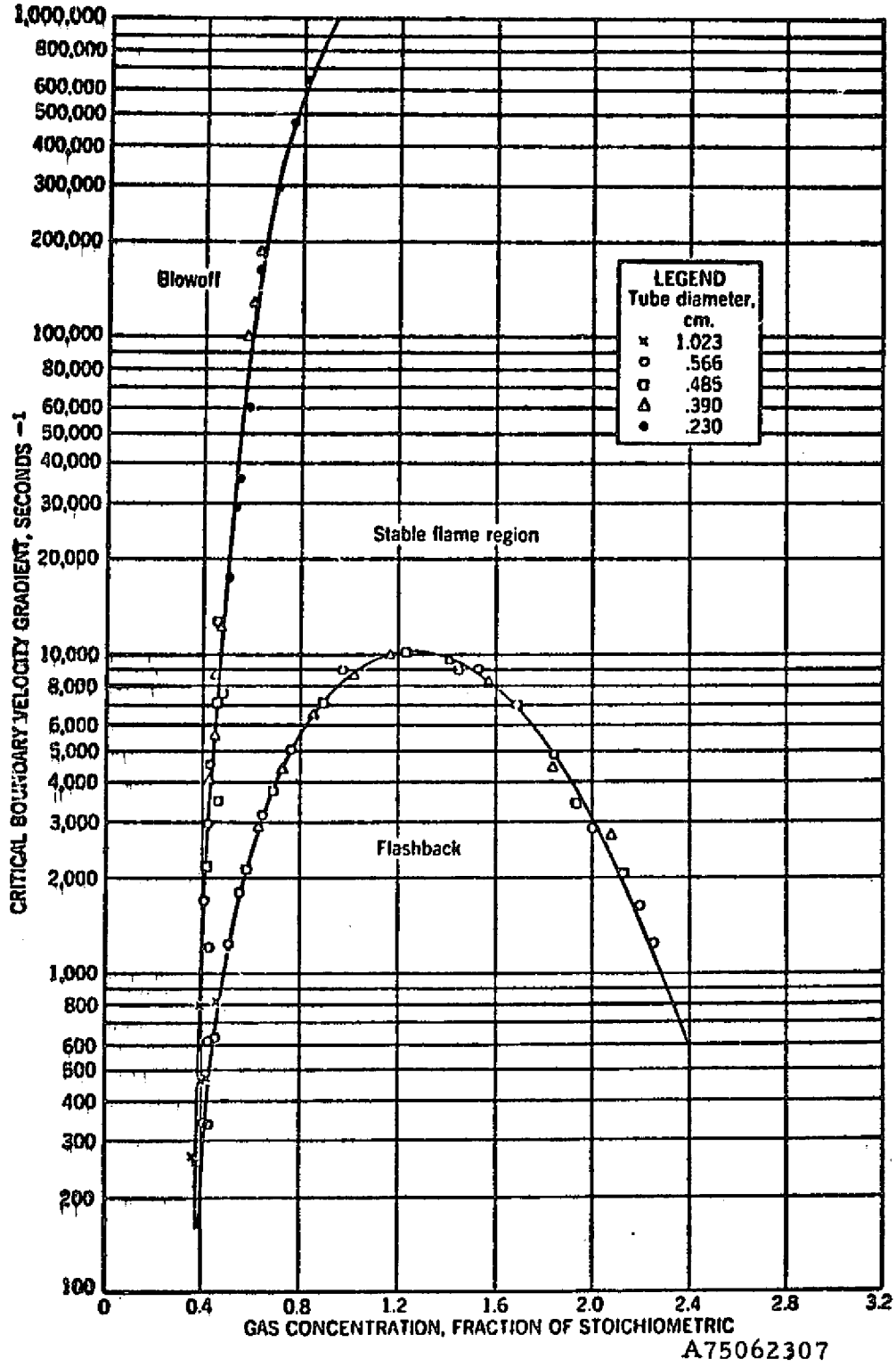

Figure 13-14. FLAME-STABILITY DIAGRAM FOR A FUEL CONTAINING 99.7% HYDROGEN AND 0.3% OXYGEN [8]

of the hydrogen through the burner ports must be 9 times greater than that of the methane. (The port gas velocity could be increased either by increasing the upstream pressure or by decreasing the port diameters.)

The problem of flashback in the conversion of natural gas appliances to hydrogen can be treated in two ways. One way is to simultaneously increase the upstream pressure and decrease the port size. This can increase the flow velocity through the burner ports enough so that it is greater than the flame speed. The other method is to decrease the amount of primary air so that the mixture upstream of the burner ports is not flammable. This second technique has been evaluated experimentally at IGT with mixed, but generally favorable, results (as discussed below).

Contemporary Atmospheric Burners Without Primary Air

A feasibility investigation was conducted using hydrogen as the fuel for a 12,000 Btu/hr (natural gas) atmospheric range-top burner. The burner head was constructed of stamped aluminum. The outlet pressure of the gas appliance regulator was factory adjusted to be 6 inches water column (approximately 0.217 lb/sq in.). The only mechanical adjustment to the burner was the sealing of the air shutter so that the burner was unable to inject primary air by entrainment. The results of the feasibility study were that —

- The aluminum range-top burner rated at 12,000 Btu/hr (0% primary air, 100% secondary air) did operate in a cooking situation— i.e., it heated approximately 4 pounds of water in a glass container (coffee pot) from approximately 68° to 212°F. Heat-transfer and energy measurements were not taken.
- The burner-head temperature was warmer to the touch of the investigator when hydrogen was used as the fuel than when natural gas was used. However, no quantitative measurements were taken.

The flames appeared to burn within the burner ports. Because flame speed is a function of gas temperature and pressure, an increase in gas temperature can change the flammability limits of a gas; and, with hydrogen, the change can cause the fuel (hydrogen) to burn within the ports.[3]

The calculated theoretical (adiabatic) flame temperature, for a stoichiometric hydrogen-air mixture and at an inlet gas temperature of 60°F, considering dissociation, is approximately 3525°F.[18] The flame temperature of a hydrogen-air mixture is, therefore, approximately only 10% higher than the

flame temperature of a natural gas-air mixture, and this difference is probably not sufficient to produce a sensible difference. However, if the specific flame intensities* of hydrogen and natural gas at stoichiometric mixtures are compared, where

$$I_{H_2} = 4.14 \text{ Btu/s-sq in.}^{12}$$

and

$$I_{Nat.} = 0.646 \text{ Btu/s-sq in.}^{13}$$

the specific flame intensity of the hydrogen-air mixture (I_{H_2}) is seen to be approximately 600% greater than that of natural gas ($I_{Nat.}$). For a gas-air mixture burned without primary air, the mathematical expression for flame intensity could be a qualitative indication of the flame-to-burner head heat transfer and of the heat available from the flame — thus possibly explaining why the burner head felt hotter to the investigator when the fuel was hydrogen.

Noise was generated upon burner start-up (ignition) and shutdown (extinction). The ignition noise was a sharp, cracking sound, whereas the extinction noise was a muffled sound of higher intensity than the ignition noise. On extinction of the burner, the noise was due to flashback occurring at a zero gas-flow rate. At ignition, the conditions favorable for the generation of noise were the ignition velocity (flame speed) of the hydrogen-air mixture and the composition of the mixture itself. There was no noise generated by the combustion waves during burner operation.

---

*Specific flame intensity of a fuel gas can be defined as the rate of heat release by the flame of this gas when burned in a prescribed burner of definite design and at a definite inner-flame-cone height. This can be expressed mathematically as[3] —

$$I = H\nu/A \qquad (13\text{-}15)$$

where —

I = the specific flame intensity (capacity) in Btu/s-sq in. port area

H = the net heating value in Btu/cu ft of gas-air mixture issuing from the burner in 1 second

ν = the rate of flame propagation of the gas-air mixture in ft/s

A = the ratio of the burner area to the inner-flame cone area.

Emissions From Hydrogen-Fueled Burners

Currently, the American National Standards Institute (ANSI) has only one criterion for combustion pollutants from domestic gas appliances, and that is in regard to carbon monoxide. The maximum quantities of carbon monoxide allowed by ANSI are shown in Table 13-13.

Table 13-13. ANSI CARBON-MONOXIDE LEVEL RESTRICTIONS

Appliance	Amount of Air-Free Carbon Monoxide, ppm
Ranges	800
Refrigerators	300
Others	400

Because hydrogen contains no carbon, its products of combustion contain no carbon monoxide or unburned hydrocarbons. However, laboratory investigators have shown[1] that an open-flame hydrogen burner produces significantly larger quantities of nitrogen oxides than an equivalent unit burning natural gas. Table 13-14 shows the nitrogen-oxides emissions from hydrogen used in an atmospheric, open-flame range burner. It should be noted that natural gas used in the open-flame burner had nitrogen-oxides emission levels of from approximately 80 to 100 ppm. From Table 13-14 it should also be noted that there was an increase of approximately 30% in nitrogen oxides emissions using secondary air only compared with using hydrogen with primary air to fuel the open-flame range burner.

Table 13-14. NITROGEN-OXIDES EMISSIONS FROM AN OPEN-FLAME RANGE BURNER USING HYDROGEN AS FUEL

	Air Shutter	
	Fully Open	Closed
Nitrogen Oxides, ppm	257	335
Increase (Maximum) Compared With Natural Gas, %	221	319
Increase (Minimum) Compared With Natural Gas, %	157	235

Discussion

The most serious shortcomings of unmodified burners operated on hydrogen rather than natural gas, with respect to the criteria previously listed, will be flashback and noise. Another problem, not related to current burner requirements, will be the generation of nitrogen oxides.

There does not appear to be a simple way to change existing burner heads so that flashback will not be a problem. Burner ports can be enlarged by drilling (as they were when manufactured gas was replaced by natural gas), but reduction of the port size is not possible. The second way of overcoming flashback tendencies, which is by eliminating the primary-air supply, seems to lead to noise generation in burners (designed for use with natural gas), which have a large cavity upstream of the burner ports for gas-air mixing.

It would appear, then, that the easiest way to convert an existing natural gas appliance for operation with hydrogen would be to design a new burner head that could be installed in the field. Such a burner head could be designed to operate without primary air (the burner ports acting as the metering orifices), and the amount of gas available for "explosions" upon flame extinction could be minimized.

Replacement Burners

Burner-Head Port Sizing

A standard-sized burner head, 9000 Btu/hr, will pass about 9 cu ft of natural gas and 47.3 cu ft of air per hour. A replacement hydrogen burner head, operated without primary air, must pass 27.7 cu ft of hydrogen to deliver heat at the same rate. Because the burner ports will be the metering orifices, the pressure upstream of the ports will be the distribution line pressure (about 7 in. wc). If we assume that eight ports are used per burner head (as in Figure 13-15), their size can be calculated from Bernoulli's theorem (Equation 13-2):

$$A = \frac{YC\,(h_L/\rho)^{0.5}}{q} \qquad (13\text{-}16)$$

$$A = 0.000296 \text{ sq in.}$$

corresponding to a diameter of 0.0097 inch.

Burner Configuration

Figure 13-15 is a suggested configuration for a hydrogen replacement burner for a range top or an automatic hot-water storage heater. An oven burner could be of long cylindrical design. However, because the anticipated small port areas may be prone to clogging by dust particles, a target or spider-type cover may be necessary to prevent blockage of the ports by foreign particles.

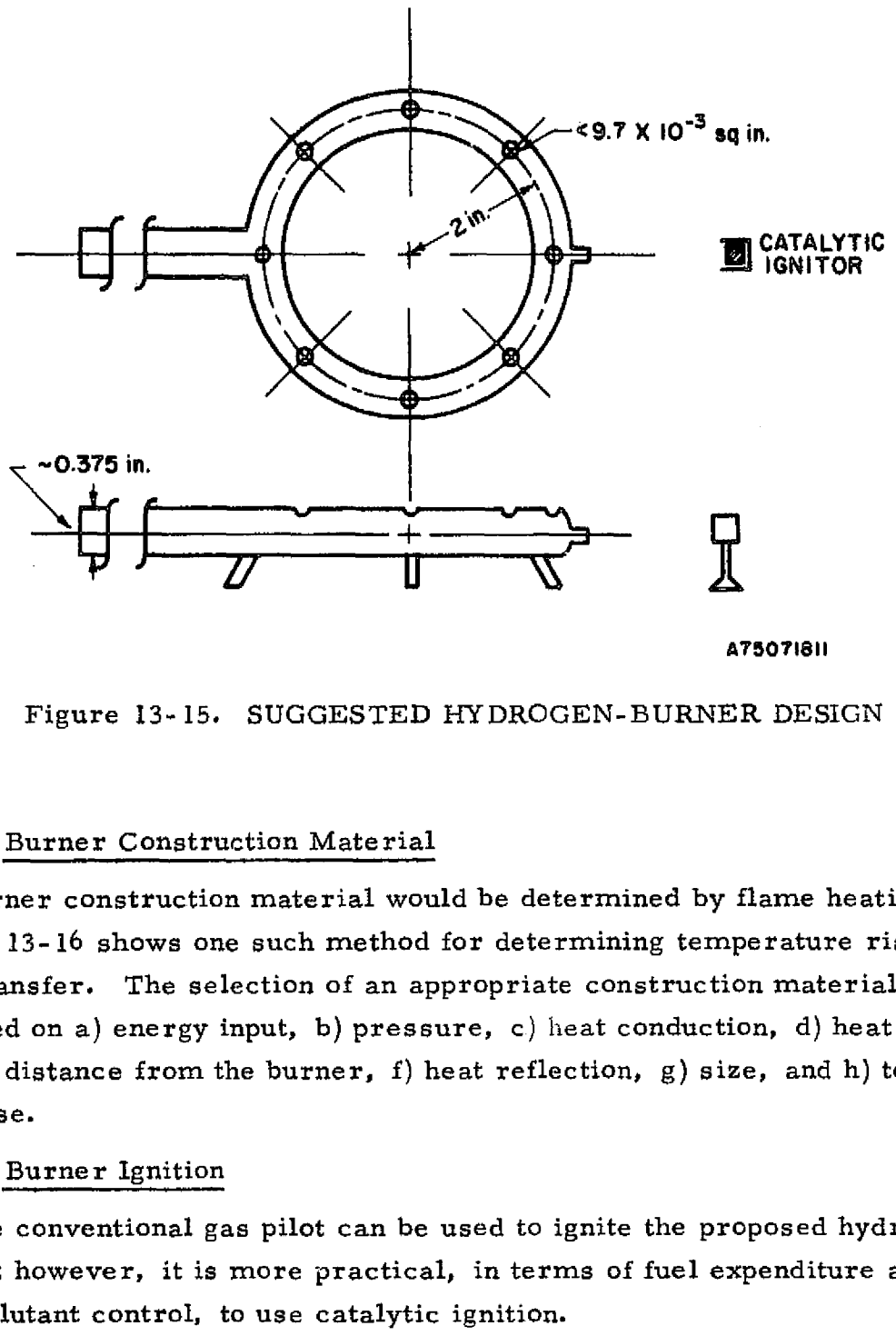

Figure 13-15. SUGGESTED HYDROGEN-BURNER DESIGN

Burner Construction Material

Burner construction material would be determined by flame heating tests. Figure 13-16 shows one such method for determining temperature rise and heat transfer. The selection of an appropriate construction material would be based on a) energy input, b) pressure, c) heat conduction, d) heat radiation, e) load distance from the burner, f) heat reflection, g) size, and h) temperature rise.

Burner Ignition

The conventional gas pilot can be used to ignite the proposed hydrogen burner; however, it is more practical, in terms of fuel expenditure and air-pollutant control, to use catalytic ignition.

In catalytic-ignition systems, the initial flow of gas (hydrogen) to the appliance passes over a catalyst. The catalyst causes the hydrogen to react with the oxygen in the air at room temperature and thereby produces heat.

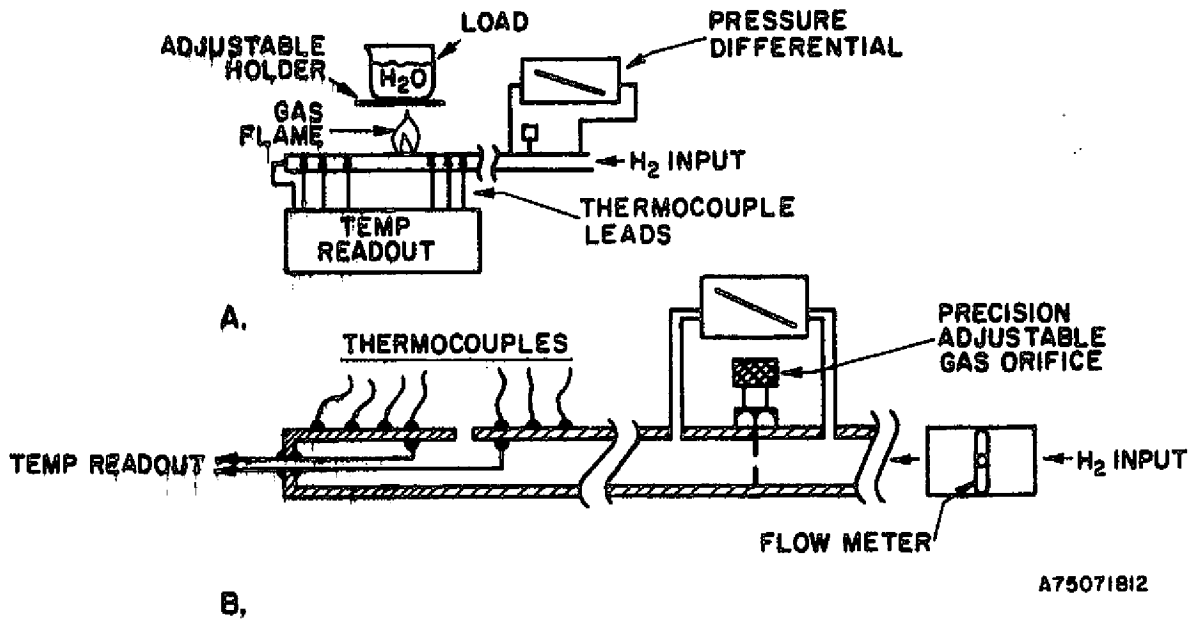

Figure 13-16. METHOD FOR CONDUCTING HYDROGEN-FLAME HEATING TESTS

The catalyst is supported on a material that heats quickly during the catalytic combustion. When the surface temperature reaches the autoignition temperature of the hydrogen-air mixture (about 1085°F), a flame is initiated.

Noise

The ignition noise will not be completely eliminated because of the anticipated concentration of hydrogen in the vicinity of the burner ports and the ignition. There should be a minimum amount of burner operation noise. The extinction noise generated by the hydrogen burner should be less than that generated by the contemporary range burner used in our feasibility investigation.* The reduction could be accomplished by a reduction in the available volume of hydrogen in the burner head at shutoff — i.e., the hydrogen burner would have less interval volume than the contemporary atmospheric gas-appliance burner.

* The extinction noise generated by the contemporary natural gas burner operating on hydrogen was found to be objectionable.

Appliance Regulators

Appliance regulators maintain a constant input pressure to the appliance, regardless of fluctuations in the supply pressure, and thus help to ensure optimum burner performance. In general, pressure regulators on domestic gas appliances use a vent for air movement from the atmospheric side of the regulator diaphragm. The working parts of such a domestic appliance regulator are shown in Figure 13-17.

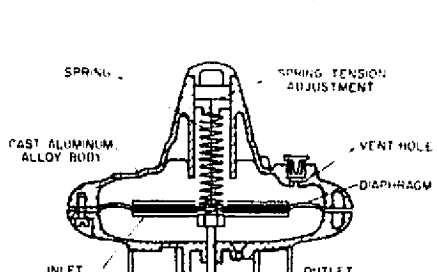

Figure 13-17. APPLIANCE REGULATOR
(Source: Rockwell Manufacturing Co.)

ANSI Standard No. Z21.18-1969 (Standard for Gas-Appliance Pressure Regulators) regarding external leakage would apply to a regulator handling hydrogen fuel. The leakage performance test uses clean air as the gas. However, the area of the vent hole appropriate for natural, manufactured, mixed, and LP gas-air mixtures (sp gr of approximately 0.64, air = 1) would be too large for use with hydrogen. The maximum allowable venting rate, as specified in ANSI Z21.18-1969 for fuel gases of specific gravities approximately equal to 0.64, is 2.5 cu ft/hr.

The lower flammability limit for natural gas (at 1 atm) is approximately 4.9%, by volume, in air.[5] For hydrogen, the lower flammability limit (at 1 atm, 72°F) is approximately 4.0%, by volume, in air.[11] If we assume that the flow rate (2.5 cu ft/hr) is such that in a well-ventilated room the lower explosion limit (LEL) for natural gas — i.e., 4.9%, by volume — is not reached, the amount of hydrogen (sp gr of 0.07, air = 1) that could be vented under these conditions would be approximately 2.0 cu ft/hr. However, approximately 7.0 cu ft of hydrogen per hour would pass through the vent sized (restricted) for natural gas. A smaller sized vent, appropriate for

hydrogen, could easily be blocked by foreign particles (dirt). There are, however, vents available with check valves that allow free movement of air into the upper diaphragm chambers, but that restrict the outward flow rate of hydrogen to some designated value. Informed opinion[7] is that residential gas appliance regulators designed to regulate natural, manufactured, and mixed gases would accommodate hydrogen without deterioration of the diaphragm or other working components.

Development of Catalytic Appliances

It is possible to design appliances that combust hydrogen through the action of a catalyst, despite the fact that efforts to develop similar burners for methane have been unsuccessful.

Catalytic combustion takes place on an active surface. Because the surface is a participant in the chemical-reaction sequence of combustion, the "energy barrier" between the reactants and products of combustion can sometimes be reduced. This allows the reactions to take place at temperatures below those characteristic of flames.

Research and development on catalytic appliances is under way at Billings Energy Research Corp., Provo, Utah, under the sponsorship of the Mountain Fuel Supply Co.,[6] and at the Institute of Gas Technology, under the sponsorship of Southern California Gas Co.[17] Billings Energy Research Corp. recently converted the cooking appliances in a Winnebago motor home to catalytic hydrogen combustion. The research at IGT is concerned with the development of catalytic ranges, water heaters, and space heaters. Catalytic-igniter research, sponsored by several gas utility companies, is also under way at IGT.

There are two differing approaches to the design of hydrogen-fueled catalytic appliances. One is to design for pure catalytic combustion, wherein all combustion takes place through the action of a very active catalyst. The other is to use a flame to heat and assist a less active catalyst.

Low-Temperature Catalytic Appliances

When catalyzed by noble metals, hydrogen combustion in air can begin at room temperature. Heat is released as the hydrogen burns, thus raising the temperature of the catalyst and substrate; but combustion can be maintained

at comparatively low (surface) temperatures. Most other common fuels must be heated to moderately high temperatures before they will begin to combust catalytically.

A low-temperature catalytic burner must maintain a steady rate of heat release to the load or to the environment so that it does not provide an ignition source for a flame. As was presented in the last section, it is quite possible to make catalytic igniters in which the combustion on the catalytic surface heats the catalyst to a temperature above the autoignition temperature of the mixture, thus initiating flame-type combustion. Stable catalytic combustion can be maintained if any of the three following criteria are met:

1. The laminar flow velocity of the hydrogen-air mixture over the catalyst is greater than the flame velocity of hydrogen. If this is true a flame cannot propagate away from the catalyst. This approach has been tested experimentally and was found to be impractical.[17]

2. The composition of the hydrogen-air mixture passed over the catalyst places the mixture beyond the limits of flammability. This approach is impractical if the mixture is fuel rich because it implies that unburned hydrogen will be vented by the appliance. Results of experiments with mixtures that are less than 4% hydrogen (fuel lean) have not been promising.[6]

3. No points on the surface of the catalyst ever reach the autoignition temperature of hydrogen-air mixtures (1085°F). This implies that a balance between the heat transferred away from the surface and the heat released by the combustion of incoming hydrogen is struck at a lower temperature.

Experiments at IGT have shown the third method to be the most practical.[17] Stable and complete catalytic combustion has been maintained in burner configurations at temperatures as low as 400°F (the surface temperature as determined by thermocouple measurements).

High-Temperature Catalytic Burners

At elevated temperatures, some materials that are not active catalysts for hydrogen combustion at low temperatures become active. Examples of such materials are iron and steel. Exploitation of this property by Billings Energy Research Corp. has resulted in a hybrid, flame-assisted catalytic burner. The configuration of this burner is shown in Figure 13-18.

During operation, the flame-assisted catalytic burner must be activated by an outside ignition source, such as a glow coil or a pilot light. At first,

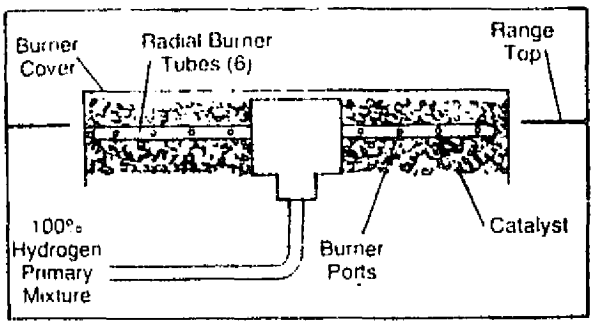

Figure 13-18. CONFIGURATION OF BILLINGS ENERGY RESEARCH CORP. FLAME-ASSISTED CATALYTIC BURNER[6]

all combustion takes place in the flame; but as the flame heats the catalytic surface, proportionately more and more combustion takes place through the action of the catalyst.

Advantages of Catalytic Combustion

It should be noted that the designing of catalytic burners is not an exact science, and a great deal of development work must be done before such devices can be marketed. The incentives for undertaking such programs are clear from the results of the first experiments performed on early burner models. Catalytic appliances can be significantly more efficient than flame burners and can virtually reduce emissions to zero.

When catalytic combustion takes place at temperatures below 1500°F, the formation of nitrogen oxides is, for all practical purposes, eliminated. Because no carbon monoxide is formed during hydrogen-air combustion, the only product of combustion is water vapor. Laboratory results of nitrogen oxides emissions from two low-temperature catalytic appliances and from four high-temperature catalytic burners are shown in Table 13-15.

The data for low-temperature catalytic appliances are reported on an air-free basis, as were the measurements by the American Gas Association Laboratories reported in the previous section. This means that the measured concentrations are adjusted to exclude the dilution effect of excess air. With excess air, the nitrogen oxides concentrations would be even lower. The experimental apparatus for making such measurements is shown in Figure 13-19. Because Reference 6 does not specify whether or not the quoted

Table 13-15. NITROGEN-OXIDES EMISSIONS FROM SEVERAL CATALYTIC APPLIANCES

	Burner Type	Nitrogen Oxides, ppm
Low-Temperature Catalytic[17] *	Chimney	0.08
	Vertical fin	0.03
High-Temperature Catalytic[6]	Standard Al range	5.2
	Stainless steel, experimental	1.8
	Al oven/broiler	4.5
	Cast iron	4.0

* Reported on an air-free basis.

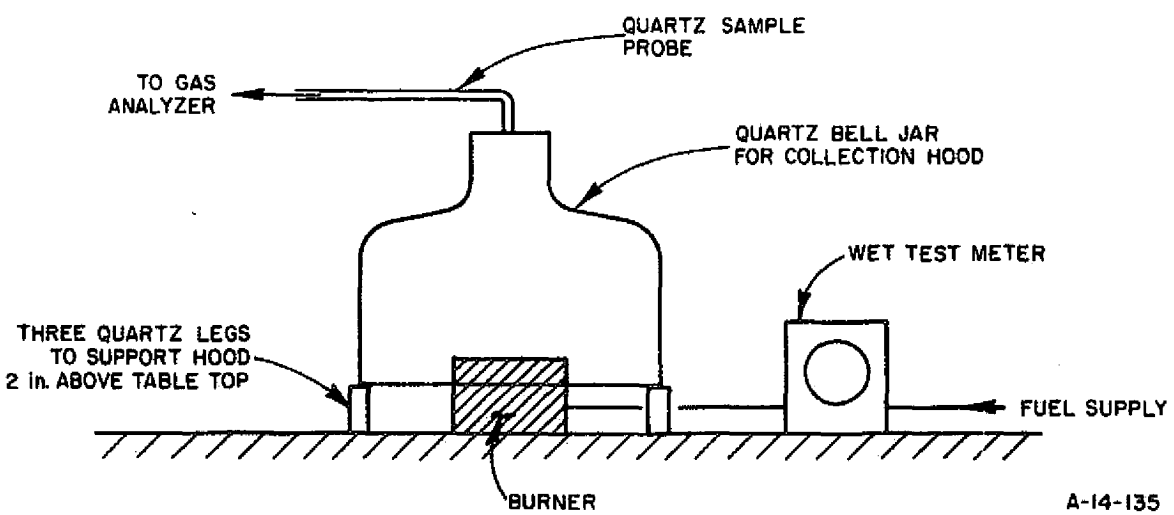

Figure 13-19. BURNER-EMISSION-TESTING SETUP

results are on an air-free basis, it is assumed that they are measured concentrations that are diluted by an undetermined amount of excess air.

The nitrogen-oxides production levels reported for the low-temperature catalytic space heaters are on about the same order of magnitude as the nitrogen-oxides levels found in ambient air. Thus it should be possible to build space heaters and other appliances that are ventless. In present-day furnaces, about 30% of the chemical energy in the fuel is lost when the com-

bustion products are vented through chimneys. Therefore, ventless appliances could potentially operate much more efficiently than present-day appliances. At IGT, under certain intermittent operating conditions, second-generation, experimental catalytic water heaters have had measured efficiencies of greater than 80%, based on that portion of the high heating value of hydrogen that is transferred to the water.

Preliminary calculations indicate that the water formed as a combustion product in ventless space heating may or may not be a problem, depending on the tolerable humidity level and the frequency of air changes in specific houses.[17] There is also the possibility with some appliances (water heaters, for example) of installing condensing units to trap combustion-produced water vapor. These traps would then permit full utilization, by the appliance, of the higher heating value of the hydrogen burned, and they would provide a supply of relatively pure water.

Cost of Catalytic Appliances

The cost of high-temperature catalytic appliances should not be significantly higher than that of standard appliances because the only addition is a stainless-steel pad. Although low-temperature catalytic appliances make use of expensive metals (such as platinum), the catalyst-loading levels are so low that the appliance price should not increase significantly. (Preliminary estimates are that only about 10¢/1000 Btu-hr would be attributable to the catalyst material.) From Table 13-3, the estimated peak-day natural gas requirements for a 1200-sq-ft house is about 1.5 million Btu. The release of this much energy by the catalytic combustion of hydrogen would then require an investment of only $12 attributable to platinum catalyst material. This figure is conservative (high) because ventless catalytic burners will be more energy efficient than standard burners and because low-temperature appliances will not need pilot lights.

References Cited in This Section

1. American Gas Association's Cleveland Laboratory, private communication of January 1975.

2. American Gas Association, "American National Standard for Household Cooling Gas Appliances," Am. Natl. Stand. Inst. Z21.1-1974. Arlington, Va., 1974.

3. American Gas Association, Gas Engineers Handbook. New York: Industrial Press Inc., 1969.

4. American Gas Association Laboratories, "Influence of Port Design and Gas Composition on Flame Characteristics of Atmospheric Burners," Res. Bull. No. 77, (1958) February.

5. American Gas Association, Gaseous Fuel – Properties, Behavior, and Utilization, 2nd Ed. New York, 1954.

6. Baker, N. R., "Oxide of Nitrogen Control Techniques for Appliance Conversion to Hydrogen Fuel." Paper presented at the Ninth Intersociety Energy Conversion and Engineering Conference, San Francisco, August 1974.

7. Dufour, R. J., Consultant to IGT.

8. Grumer, J., Harris, M. E. and Rowe, V. E., "Fundamental Flashback, Blowoff, and Yellow-Tip Limits of Fuel Gas-Air Mixtures," U.S. Bur. Mines Rep. Invest. 5225. Washington, D.C.: U.S. Department of the Interior, 1956.

9. Hittman Associates, Inc., Residential Energy Consumption. Columbia, Md., n.d.

10. Industrial Heating Equipment Association, Combustion Technology Manual, 2nd Ed. Washington, D.C., 1974.

11. Jones, G. W., U.S. Bur. Mines Tech. Pap. No. 450. Washington, D.C.: U.S. Department of the Interior, 1929.

12. Ladenburg, R. W. et. al., Eds., Physical Measurements in Gas Dynamics and Combustion, 409-38. Princeton, N.J.: Princeton University Press, 1954.

13. Lewis, B. and von Elbe, G., "Stability and Structure of Burner Flames," J. Chem. Phys. 11, 75-79 (1943).

14. Lewis, B. and von Elbe, G., Combustion Flames and Explosions of Gases. New York: Academic Press, Inc., 1951.

15. Mason, D. M. and Eakin, B. E., "Calculation of Heating Value and Specific Gravity of Fuel Gases," Inst. Gas Technol. Chicago Res. Bull. No. 32, (1961) December.

16. Northern Natural Gas Co., Residential-Appliance Gas Consumption, Omaha, September 1970.

17. Sharer, J. C. and Pangborn, J. B., "Utilization of Hydrogen as an Appliance Fuel." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami Beach, March 18-20, 1974.

18. The North American Manufacturing Co., North American Combustion Handbook. Cleveland, 1952.

14. HYDROGEN AS A FEEDSTOCK FOR SYNTHETIC FUEL PROCESSES – T. D. Donakowski and J. C. Gillis

From the conclusions presented in the previous sections, it should be clear that hydrogen will be an expensive commodity and as such will not find much use as a fuel in the immediate future, but will be a valuable chemical feedstock. We have reviewed some of the ways present-day industries could use feedstock hydrogen, but have not yet commented on an industry, developing in the mid to long term, that has the potential to become a large market for feedstock hydrogen – the synthesis of clean fuels from coal and oil shale.

The fundamental objective of all coal-based synthetic fuels processes is to turn a low hydrogen-content fuel (coal) into high hydrogen-content fuels (oils, methanol, and methane). Hydrogen is currently produced from coal during these processes; in some processes, a great deal of the input coal (in the methanol process, about half) is used for hydrogen production.

At present, onsite hydrogen production from coal is the cheapest process available. However, coal is an exhaustible resource, the price of which will surely rise in the long term. There are possible sources of hydrogen that are tied to renewable or extremely large energy sources (solar or nuclear), which are not likely to rise as much in cost as fossil fuels in the long term. Thus, it seems likely that at some point in the future it will be economically advantageous to reserve as much coal as possible for synthetic-fuels production and to utilize some "outside" source of hydrogen.

We have investigated this possibility during the course of this study. We have focused our attention on "retrofitting" developed synthetic-fuels processes to accept outside hydrogen because the synthetic-fuels industry is likely to be well established, with great investments in process-plant equipment, before outside hydrogen becomes economically attractive.

Coal Conversion to Substitute Natural Gas

Coal has a molecular hydrogen-to-carbon ratio of about 0.8, but in methane the hydrogen-to-carbon ratio is 4. Thus, coal-to-substitute natural gas (SNG) processes are really "hydrogen-addition" processes.

Many processes have been proposed for the conversion of coal to SNG. They employ a gasifier-reactor to produce a combination of carbon monoxide, hydrogen, and methane in one or more stages. The principal chemical reactions taking place in the gasifier are –

$$C + H_2O \rightarrow CO + H_2$$
$$C + 2H_2 \rightarrow CH_4$$

A portion of the carbon monoxide in the gasifier product stream is often used to produce hydrogen in a "shift" reactor by the reaction –

$$CO + H_2O \rightarrow CO_2 + H_2$$

The carbon dioxide is then removed; and after final purification, the remaining hydrogen, carbon monoxide, and methane is sent to a "methanation" reactor. There the carbon monoxide and hydrogen are reacted to form more methane:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

and the product gas has a higher heating value, about 950 Btu/SCF.[15] The "generalized" SNG process is shown in Figure 14-1.

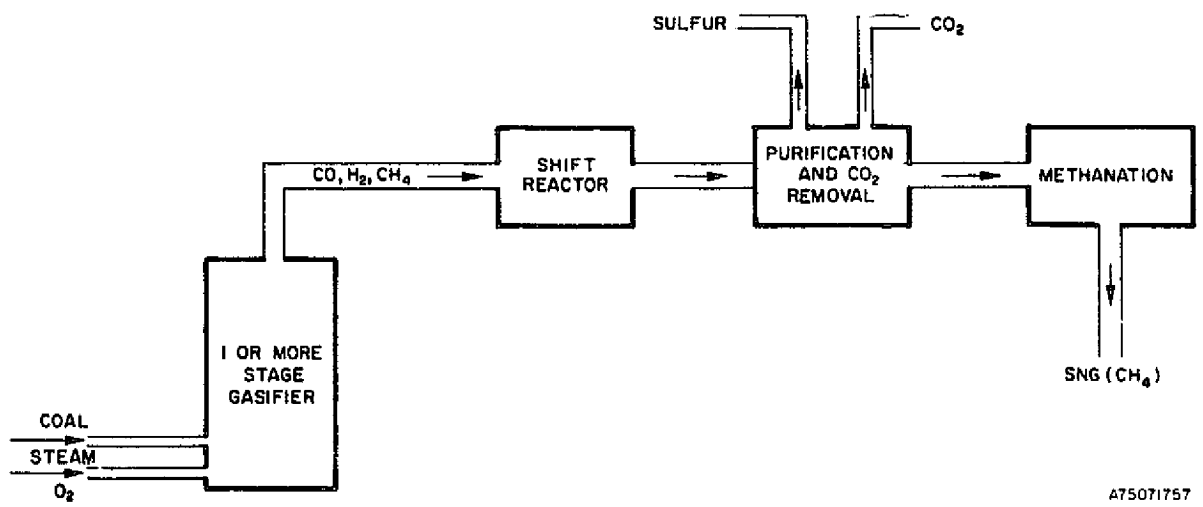

Figure 14-1. GENERALIZED SNG PROCESS

Almost all of the proposed SNG processes are of the general form presented in Figure 14-1. The differences in the processes are to be found in the approach to the first step — the gasifier. For convenience, we will divide SNG processes into groups according to the type of gasifiers they utilize: single-stage gasifiers, multistage hydrogasifiers, and other gasifiers.

The Lurgi and Koppers-Totzek SNG Processes are examples those that utilize single-stage gasification. However, the two gasifiers involved are of quite different designs and operate at different conditions. The Lurgi gasifier typically requires noncaking coal and operates at from 350 to 450 psi and at 1150° to 1400°F, producing a significant amount of methane as well as light hydrocarbon byproducts.[3] The Koppers-Totzek gasifier works with both caking and noncaking coals, but operates at near-atmospheric pressure and reaches much higher temperatures (up to 3300°F). The high temperature precludes formation of any light hydrocarbons and ensures complete gasification of almost all of the carbon matter.[7]

In both processes the synthesis gas is formed via the steam-coal reaction:

$$C + H_2O + \text{heat} \rightarrow CO + H_2$$

Water is added, in excess, to both gasifiers to partially oxidize the carbon in the coal, to serve as a source of hydrogen itself, and to act as a temperature moderator for the reactor. Some of the water is eventually used to generate more hydrogen in the shift reactor.

Heat for the steam-coal reaction is provided by combusting part of the coal with oxygen. High-purity oxygen is used to prevent dilution of the product stream with the nitrogen present in air.

As the name implies, multistage hydrogasifiers are those that involve two or more stages, in one or more vessels, in gasifying coal. (See Figure 14-2.) In general, the initial stage devolatilizes the coal and forms methane or synthesis gas. Greater heating efficiency can be obtained by the direct formation of methane in the gasifier. Heat from the methane-forming reactions can then be more effectively absorbed in situ to expedite the steam-coal reaction and to devolatilize the coal.[27] The methane reactions are —

$$C + 2H_2 \rightarrow CH_4 + \text{heat}$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O + \text{heat}$$

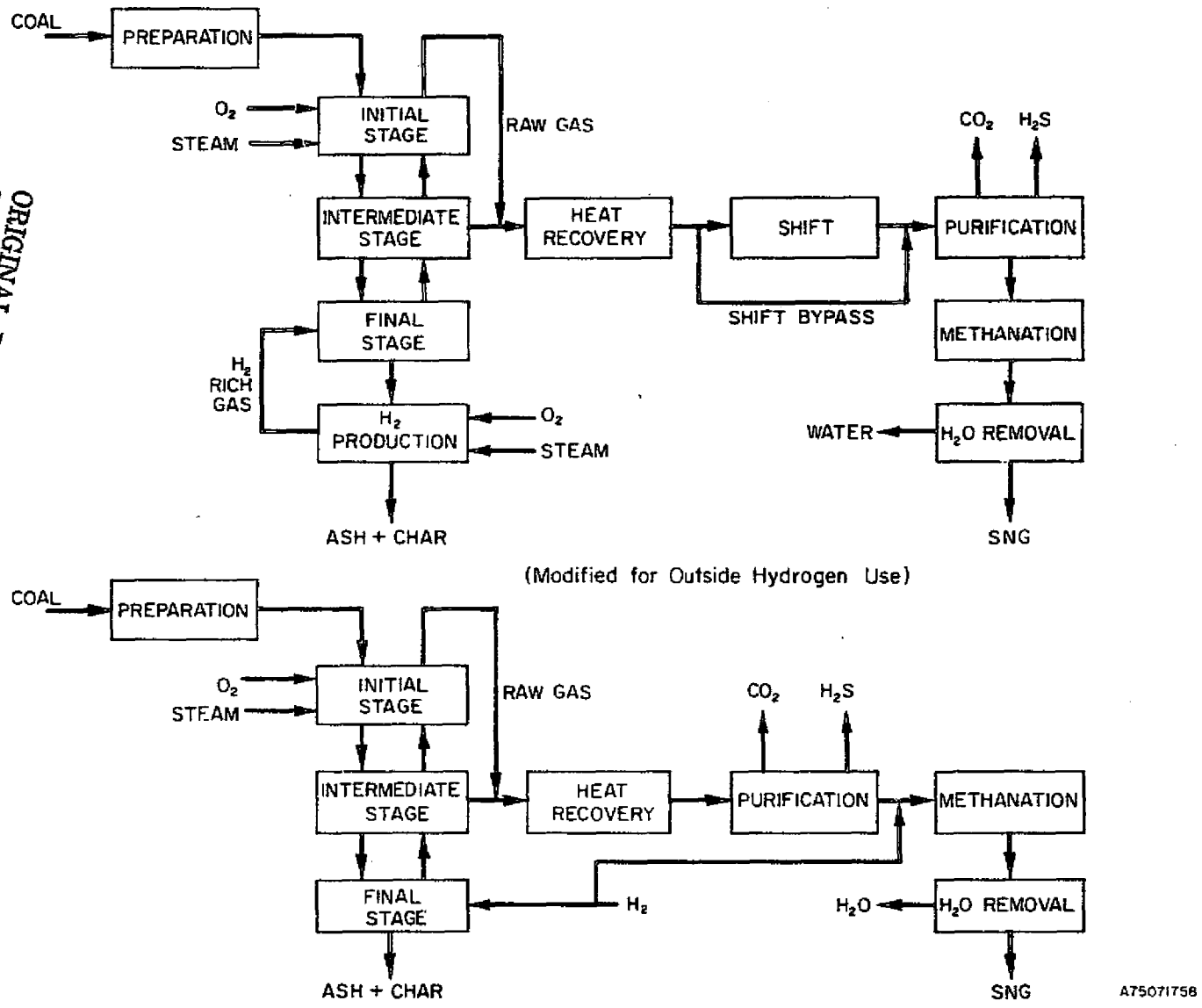

Figure 14-2. SNG PRODUCTION
(Multistage Hydrogasification Process)

The steam-coal reation is —

$$C + H_2O + \text{heat} \rightarrow CO + H_2$$

The hydrogen required for the hydrogasification step is produced in the final stage of the gasifier by the partial oxidation of char to form a hydrogen-rich synthesis gas.

Having thus produced a raw gas, the stream is cooled; shifted, if necessary, to increase the hydrogen/carbon monoxide ratio to that required for methanation; purified of carbon dioxide and hydrogen sulfide; and, finally, methanated to reduce the carbon monoxide content and to yield the SNG product.

The other gasification process schemes utilize novel features in their coal-gasification steps. The ATGAS Process uses molten iron to gasify the coal and to produce a carbon monoxide-rich synthesis gas that contains no methane. Because no methane is produced in the gasifier, a considerable amount of carbon monoxide must be shifted to obtain hydrogen for eventual synthesis to methane. The Kellogg Process uses a molten salt (sodium carbonate) as the medium for coal gasification. The salt catalyzes the steam-coal reaction and also acts as a good heat-transfer agent. The synthesis gas is shifted to produce the proper composition for methanation. Another special gasification method is the CO_2 Acceptor Process. Coal is gasified in a two stage reactor, with the required process heat supplied by the exothermic reaction of carbon dioxide with calcium oxide, forming calcium carbonate. Enough hydrogen is produced in the gasifier from the steam-coal reaction so that a shift reaction prior to methanation is not required.[3] Gasifier operating conditions and R & D statuses for SNG production are summarized in Table 14-1.

The water-gas shift reaction is an important step in almost all gasification processes. The reaction is required to increase the hydrogen/carbon monoxide ratio to that necessary for methanation, about 3.6:1. The shift reaction is —

$$CO + H_2O \rightarrow CO_2 + H_2 + \text{heat}$$

It consumes water, reducing it to hydrogen and oxygen and oxidizing the carbon monoxide produced from coal to carbon dioxide. The carbon dioxide is more difficult to convert to methane and is scrubbed from the system, along with hydrogen sulfides prior to methanation.[22] The carbon in the carbon dioxide was originally present in the coal, so that by removing

Table 14-1. COAL-TO-SUBSTITUTE NATURAL GAS PROCESSES

Process	Gasifier Conditions	R&D Status
Single-stage gasifiers		
Koppers-Totzek[4]	Any type coal, 2700°F, atmospheric pressure	16 plants in operation, methanation step not demonstrated
Lurgi[3, 15, 22]	Noncaking coal, 1300°F 400 psi	58 plants have been constructed since 1936; methanation step not demonstrated; commercial design, including methanation, completed by Fluor Engineering
Multistage hydrogasifiers		
BI-GAS[3, 30]	First stage, 2700°F; second stage, 1700°F; 1000 psi	120 tons of coal/day pilot plant scheduled for completion fall 1975
Hydrane[15, 30]	Direct reaction with hydrogen, 1650°F, 1000 psi	10 pounds of coal/hr pilot plant has been operated, design of 24 tons/day pilot plant under way
HYGAS®[5]	Direct reaction with hydrogen; first stage, 1250°F; second stage, 1750°F; 1000 psi	75 tons of coal/day pilot plant in operation since 1971
Synthane[15, 30]	1800°F, 1000 psi	75 tons of coal/day pilot plant essentially completed and operations starting
Special gasifiers		
ATGAS[15]	Reaction in bath of molten iron, 2500°F, near atmospheric pressure	Bench-scale studies completed
CO_2 Acceptor[15, 30]	No oxygen required, 1500°F, 150 psi	30 tons of coal/day pilot plant in operation, methanation step in start-up
Kellogg Molten Salt[15]	Bath of molten sodium carbonate, 1700°F, 1200 psi	Bench-scale testing

and venting the carbon dioxide from the system, a great deal of raw-material carbon is lost.

The final step in producing the methane for use as pipeline gas is the catalytic combination of carbon monoxide and hydrogen to form methane and water by the methanation reaction —

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

This reaction has only recently been tested on a commercial scale with the carbon monoxide concentrations as high as is typically expected. [18]

Methanation is used in some chemical processes today (e.g., in ammonia synthesis), but only in applications in which the methane-forming reactants (carbon monoxide, carbon dioxide and hydrogen) are diluted with large concentrations of nonparticipating gases. [33] Methanation of gas streams in which essentially all incoming gases participate in the reactions is still under development. The main difficulty is the removal of the large quantities of heat released in the catalytic reactor by methane formation. [20] An alumina-supported nickel catalyst is usually designed to operate in a temperature range of from 500 °to 650 °F, so adequate temperature control within the reactor is essential. The catalyst is also sensitive to sulfur poisoning. Sulfur depositions of 0.15% (by weight) are detrimental, so adequate hydrogen sulfide removal upstream is mandatory. Although the methanation step is the least-proved commercial technology in SNG production from coal, excellent progress has been made in small-scale methanation catalysts for refineries; [6] and a total, commercial coal-to-SNG plant should be fully realized in just a few years.

The generalized coal-to-SNG process (Figure 14-1) could be modified in two places to utilize outside hydrogen in the gasifier and in the shift reactor.

In processes using single-stage gasifiers, hydrogen is produced in the gasifier from steam. [3] In order to use hydrogen in the gasifier directly, an entirely new reactor design would most likely be necessary — a project outside the scope of this study. With hydrogasifiers, however, a reducing gas composed of hydrogen and carbon monoxide is used as input to the gasifier. This could be replaced with hydrogen. The use of rather pure hydrogen in the process allows for smaller volume flows compared with hydrogen-rich streams containing significant amounts of carbon monoxide and carbon dioxide.

The realization of smaller gas volumes allows for the use of smaller scale reactors and accompanying equipment. A flow diagram for conventional and modified hydrogasifiers is shown in Figure 14-2. The material balances around the gasifiers for a HYGAS® and a Hydrane Process, shown in Tables 14-2 and 14-3, indicate that the modified hydrogasifiers would use 1.1 to 1.5 SCF of outside hydrogen per SCF of SNG produced. Sufficient information for calculation on BI-GAS and Synthane Processes was not available; but, due to process similarity, hydrogen usage should fall within the same range as that calculated for the other hydrogasifiers.

In most coal-to-SNG processes a shift step is necessary before methanation. Here a stream of outside hydrogen could be directly added to accomplish the required increase in the hydrogen/carbon monoxide ratio; and, by so doing, the entire shift reactor and its catalyst could be eliminated. No carbon monoxide is shifted to produce hydrogen, so more is available for eventual conversion to methane, thereby increasing the product yield per amount of coal fed. With less carbon dioxide now in the process stream, the separation requirements are less severe. Process water requirements can also be reduced because water is not consumed by a shift reaction. (This could be accomplished by small reductions in the amount of steam injected to the gasifier.) In general, the addition of outside hydrogen to perform the hydrogen enrichment now accomplished by a shift reaction results in a much simpler operation with more effective coal utilization in forming product SNG.

The abovementioned modification was made to a Lurgi Process, which was then compared with the conventional scheme. (Figure 14-3 is the flow diagram). A material balance around the shift reactor is presented in Table 14-4 and shows that about 1 SCF of hydrogen can be used per SCF of SNG output from the modified process. A Koppers-Totzek Process was similarly modified to eliminate the shift step by using outside hydrogen. A material balance around the conventional shift step is presented in Table 14-5. Using a Koppers-Totzek gasification process the idealized hydrogen usage is about 2.4 times the volume of the SNG produced. This requirement is higher than that for a Lurgi process because virtually no methane is formed inside the Koppers-Totzek gasifier, but is produced indirectly by reacting the comparatively larger amount of carbon monoxide,

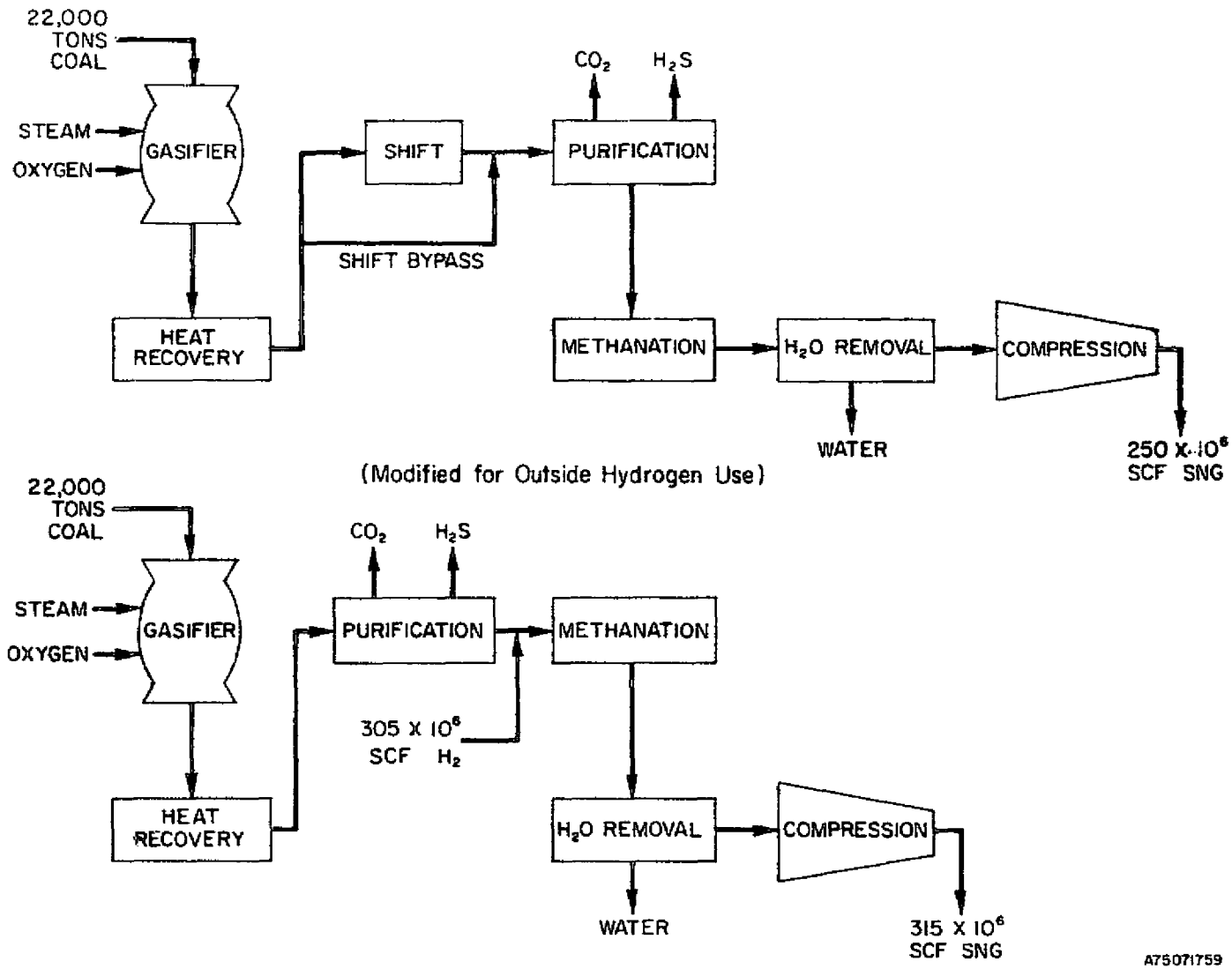

Figure 14-3. SNG PRODUCTION
(Lurgi Single-Stage Gasification Process)

Table 14-2. TYPICAL INPUT AND OUTPUT OF GASEOUS STREAMS IN FINAL STAGE OF THE HYDROGASIFIER-REACTOR, HYGAS® COAL-TO-SNG PROCESS[36]
(Hydrogen by Steam-Iron Process, 250 Million SCF/Day)

Component	Hydrogen-Rich Gas Feed	Gasifier Effluent
	Vol % (Dry)	
Carbon Monoxide	0	12.6
Hydrogen	100	51.6
Carbon Dioxide	0	9.2
Methane	0	23.7
Hydrogen Sulfide	0	1.7
Ethane	0	0.8
Other	0	0.4
Total	100	100.0
10^6 SCF/DAY	279	355

Amount of Externally Generated Hydrogen Used in Process —

$$1.0 \times 279 \times 10^6 \text{ SCF} = 279 \times 10^6 \text{ SCF}$$

Volumetric Ratio of Outside Hydrogen to SNG —

$$\frac{279 \times 10^6}{250 \times 10^6} = 1.1, \text{ or } 110\%$$

Table 14-3, TYPICAL INPUT AND OUTPUT OF GASEOUS STREAMS IN GASIFIER-REACTOR, HYDRANE COAL-TO-SNG PROCESS[38] (250 Million SCF/Day)

Component	Hydrogen-Rich Gas Feed	Gasifier Effluent
	Vol % (Dry)	
Carbon Monoxide	0	3.9
Hydrogen	100	22.9
Carbon Dioxide	0	0
Methane	0	73.2
Total	100	100.0
10^6 SCF/Day	365	283

Amount of Externally Generated Hydrogen Used in Process —

$$1.0 \times 365 \times 10^6 \text{ SCF/Day} = 365 \times 10^6 \text{ SCF/Day}$$

Volumetric Ratio of Outside Hydrogen to SNG —

$$\frac{365 \times 10^6}{250 \times 10^6} = 1.5, \text{ or } 150\%$$

Table 14-4. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, LURGI COAL-TO-SNG PROCESS[22] (250 Million SCF/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	19.6	3.9
Hydrogen	38.8	46.8
Carbon Dioxide	28.9	38.2
Methane	11.1	9.6
Hydrogen Sulfide	0.3	0.3
Ethylene	0.4	0.4
Ethane	0.6	0.5
Nitrogen and Argon	0.3	0.3
Total	100.0	100.0
10^6 SCF/Day	430	490

Amount of Carbon Monoxide Shifted to Produce Hydrogen —

$$0.196 \times 430 \text{ (In)} - 0.039 \times 490 \times 10^6 \text{ (Out)} = 65 \times 10^6 \text{ SCF/Day}$$

If No Shift Is Performed —

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 65×10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide to Form Methane = $3.7 \times 65 \times 10^6$ = 240×10^6 SCF/Day

Total Hydrogen Required 305×10^6 SCF/Day

Additional Methane Produced (Equals Carbon Monoxide Not Shifted) = 65×10^6 SCF/Day

Volumetric Ratio of Outside Hydrogen to SNG

$$= \frac{305 \times 10^6}{(250 + 65) \times 10^6} = 0.97$$

Table 14-5. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, KOPPERS-TOTZEK COAL-TO-SNG PROCESS[7] (250 Million SCF/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	55.9	17.5
Hydrogen	37.4	52.8
Carbon Dioxide	6.0	29.1
Methane	0.0	0.0
Nitrogen	0.7	0.6
Total	100.0	100.0
10^6 SCF/Day	1030	1370

Amount of Carbon Monoxide Shifted to Produce Hydrogen —

$$0.559 \times 1030 \times 10^6 \text{ SCF/Day (In)} - 0.175 \times 1370 \times 10^6 \text{ SCF/Day (Out)} = 336 \times 10^6 \text{ SCF/Day}$$

If No Shift Is Performed —

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 336×10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide to Form Methane = $3.1 \times 336 \times 10^6$ = 1040×10^6 SCF/Day

Total Hydrogen Required 1376×10^6 SCF/Day

Additional Methane Produced (Equals Carbon Monoxide Not Shifted) = 336×10^6 SCF/Day

Volumetric Ratio of Outside Hydrogen to SNG

$$= \frac{1376 \times 10^6}{(250 + 336) \times 10^6} = 2.4$$

which must be present in the synthesis gas, with the much larger amounts of hydrogen in the methanation reactor.

The special gasification processes can similarly be modified to use an outside source of hydrogen, thus eliminating the carbon monoxide shift step. The ATGAS Molten-Iron Process produces a carbon monoxide-rich synthesis gas that contains no methane. A considerable amount of carbon monoxide must be shifted to obtain the hydrogen required for methanation. When the shift reactor is removed, the process hydrogen requirement is high, about 2.7 times the volume of the SNG produced. (See Table 14-6.) The CO_2 Acceptor Process produces sufficient hydrogen internally, due in part to the in situ removal of carbon dioxide by chemical reaction, so that a shifting step is not required.[3] Because of the basic design, then, this process cannot be practically modified to the use of an outside source of hydrogen.

Coal Conversion to Low-Btu Gas

Coal may also be converted to a clean-burning, low-heat-content gas (150 to 300 Btu/SCF). By gasifying the coal, sulfur is more easily removed (as hydrogen sulfide); and the fuel burns cleaner. Low-Btu gas is produced by using air instead of oxygen in any primary coal gasifier. This eliminates the costly production of oxygen by air separation. The product stream then contains nitrogen, which lowers its heating value and makes long-distance transportation of the gas uneconomical. Hydrogen is produced within the process stream, along with carbon monoxide and some methane. With a lower heating value per volume than SNG, compression and transportation, by pipeline, of the low-Btu gas is not economical; so onsite use is preferred. The electric power industry is envisioned as the principal consumer of such gas.[15] Many of the low-Btu processes, such as Westinghouse's Clean Power Gas and IGT's U-GAS,™ are designed to be part of a combined gas-steam turbine cycle for an efficient and low-polluting electric generating plant.[12,21] A brief description and the status of various processes are presented in Table 14-7.

The low-Btu gas is produced by using air to oxidize the coal, providing heat and forming the synthesis gas, with the accompanying inert nitrogen acting as a diluent and reducing the heat content. The sulfur (as hydrogen sulfide) and particulates are removed to obtain the low-Btu product. A shift reaction is not performed.

Table 14-6. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, ATGAS COAL-TO-SNG PROCESS[19] (250 Million SCF/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	65	16
Hydrogen	35	54
Carbon Dioxide	0	30
Methane	0	0
Hydrogen Sulfide	0	0
Total	100	100
10^6 SCF/Day	1030	1460

Amount of Carbon Monoxide Shifted to Produce Hydrogen —

$$0.65 \times 1030 \times 10^6 \text{ SCF/Day (In)} - 0.16 \times 1460 \times 10^6 \text{ SCF/Day (Out)} = 436 \times 10^6 \text{ SCF/Day}$$

If No Shift Is Performed —

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 436×10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide To Form Methane = $3.3 \times 436 \times 10^6$ = 1439×10^6 SCF/Day

Total Hydrogen Required 1875×10^6 SCF/Day

Additional Methane Produced (Equals Carbon Monoxide Not Shifted) = 436×10^6 SCF/Day

Volumetric Ratio of Outside Hydrogen to SNG

$$= \frac{1875 \times 10^6}{(250 + 436) \times 10^6} = 2.7$$

Table 14-7. PROCESSES FOR CONVERSION OF COAL TO LOW-BTU GAS

Process	Gasifier Conditions	R&D Status
Koppers-Totzek[4]	Any type coal, 2700°F, atmospheric pressure	16 plants in operation
Lurgi[3, 15]	Noncaking coal, 1300°F, 400 psi	58 plants constructed since 1936
ATGAS[15]	Reaction in molten iron, 2500°F, near atmospheric pressure	Bench-scale studies completed
Synthane[10, 30]	1800°F, 300 psi	75 tons of coal/day pilot plant to produce SNG essentially completed and operations starting
U-GAS™[5]	1900°F, 300 psi	High temperature (800°F) sulfur removal (i.e., hydrogen sulfide and carbonyl sulfide) not demonstrated
Westinghouse Clean Power Gas[12]	2100°F, 150-225 psi	1/2 ton of coal/day process development unit constructed and should have started operation early this year
Winkler[15]	1500°-1800°F, atmospheric pressure	16 plants constructed since 1926

Low-Btu-gasification schemes, as currently conceived then, are not amenable to an outside source of hydrogen and would not be able to use any directly in the process.

Coal Conversion to Methanol

Coal can be converted to methanol by first forming a synthesis gas (carbon monoxide and hydrogen) via the coal-water reaction —

$$C + H_2O \rightarrow CO + H_2$$

The gas is then shifted to increase the ratio of hydrogen to carbon monoxide. The gas stream is purified, compressed, and converted to alcohol in a catalytic methanol-synthesis reactor. The methanol conversion is —

$$CO + 2H_2 \rightarrow CH_3OH$$
$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

All steps in the process involve current commercial technology, but nearly all synthesis gas for methanol conversion is now made by reforming natural gas because feedstock has been inexpensive. The reforming reaction is —

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

In coal-based methanol synthesis, a convenient gasification is the Koppers-Totzek Process because minimal methane and tar byproducts are formed. The resulting synthesis gas is shifted to provide a molecular hydrogen/(carbon monoxide and 1.5 carbon dioxide) ratio of 2.05:1.[24] Table 14-8 summarizes the development status of methanol-synthesis processes.

Outside hydrogen could be used to enrich the stream, thereby eliminating the shifting step and increasing the amount of carbon monoxide available for conversion to methanol. Figure 14-4 shows such a process. The increase in product is substantial and would more than double the amount of alcohol produced from a ton of coal. This modified process is capable of using 42,000 SCF of outside hydrogen per ton of methanol produced. (See Table 14-9.) The hydrogen-rich synthesis gas stream is then sent to a pressurized catalytic reactor for conversion to methanol. About 92% of the additional carbon monoxide can be converted to product methanol. (Losses occur because of purging of unreacted carbon monoxide and some methanol.)

C.5

Table 14-8. COAL-TO-METHANOL PROCESSES

Process	Conditions	R&D Status
Gasification step		
Koppers-Totzek[4]	Any type coal, 2700°F, atmospheric pressure	16 plants in operation*
Lurgi[3,15]	Noncaking coal, 1300°F, 400 psi	58 plants constructed since 1936*
Methanol conversion step[24]		
Imperial Chemical Industries Ltd. (Low Pressure)	480°-570°F, 1500 psi	Current commercial process
Nissui-Topsoe (Medium Pressure)	460°-450°F, 2300 psi	Current commercial process
Japan Gas Chemical Co. (High Pressure)	4300 psi	Current commercial process

* None of these plants currently manufacture methanol.

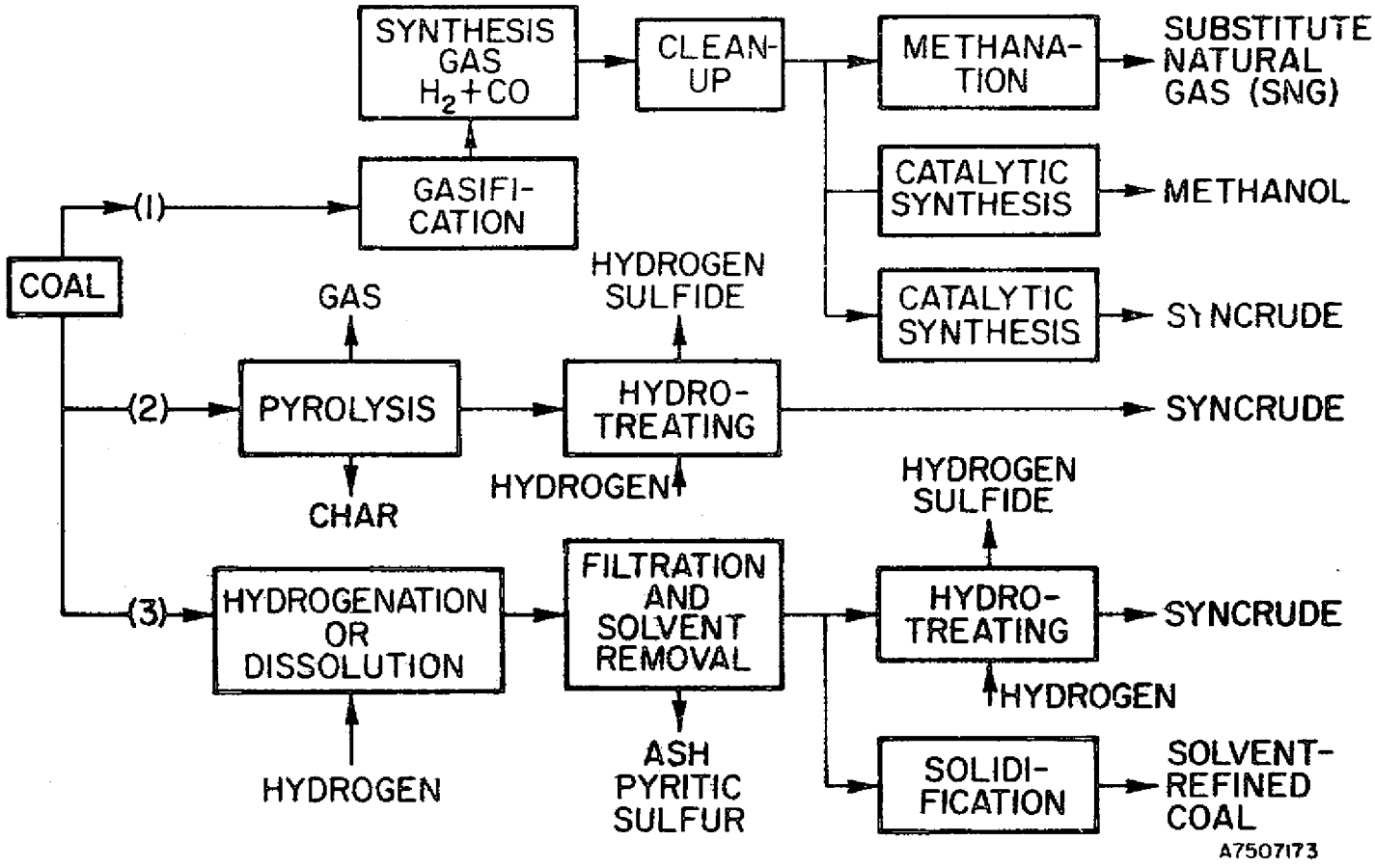

Figure 14-4. METHANOL PRODUCTION
(Koppers-Totzek Gasification and Imperial Chemical Industries Ltd. Conversion Processes)

Table 14-9. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, KOPPERS-TOTZEK AND IMPERIAL CHEMICAL INDUSTRIES COAL-TO-METHANOL PROCESSES[24]
(5000 Tons/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	56.1	17.1
Hydrogen	33.2	50.0
Carbon Dioxide	8.3	31.3
Methane	0.1	0.1
Hydrogen Sulfide	1.2	0.9
Other	1.1	0.6
Total	100.0	100.0
10^6 SCF/Day	446	598

Amount of Carbon Monoxide Shifted to Produce Hydrogen —

$$0.561 \times 446 \times 10^6 \text{ SCF/Day (In)} - 0.171 \times 698 \times 10^6 \text{ SCF/Day (Out)} = 148 \times 10^6 \text{ SCF/Day}$$

If No Shift Is Performed —

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 148×10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide to Form Methanol = $2.05 \times 148 \times 10^6$ SCF/Day = 303×10^6 SCF/Day

Total Hydrogen Required 451×10^6 SCF/Day

Additional Methanol Produced = 148×10^6 SCF of Carbon Monoxide/Day ÷ 380 SCF/lb-mol × 32 lb of Methanol/lb-mol ÷ 2000 lb/Ton × 0.92 Conversion Factor = 5700 Tons/Day

Volumetric Ratio of Outside Hydrogen to Methanol
= 451×10^6 SCF/Day ÷ (5000 + 5700) Tons/Day
= 42,000 SCF/Ton

Coal Conversion to Liquid Hydrocarbons

Coal can be transformed to conventional liquid products, such as gasoline, distillate fuels, and fuel oil, by many processes. Substantial restructuring of coal takes place, and most of the pyritic sulfur and mineral matter is removed.[18] The three routes by which coal may be liquified as shown in Figure 14-5.

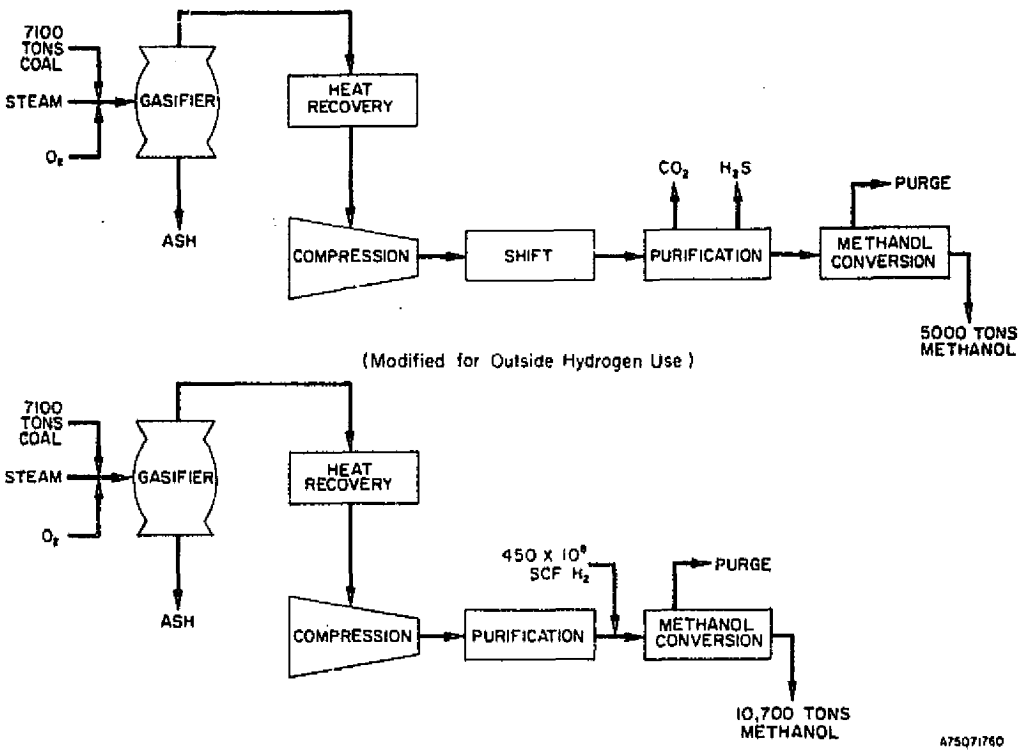

Figure 14-5. PRODUCTION ROUTES: CLEAN FUELS FROM COAL

Coal liquids can be made indirectly by gasifying the coal, converting the gas to a rich synthesis gas (carbon monoxide and hydrogen), and catalytically recombining the carbon oxides and hydrogen to form light oils. Reactors are operated at pressures from 200 to 400 psi and at temperatures from 430°to 625°F. Various amounts of gas and light liquids can be generated by operating under different conditions of conversion severity (e.g., varying catalyst activity or tailgas recycle rate).[13] This was the first technology (Fischer-Tropsch) developed for making liquid hydrocarbons from coal, and it was used in Germany during World War II.[15]

In pyrolysis processes, coal is heated to break up polymeric carbon rings in the coal and to drive out all volatile components, which are collected, condensed, and separated into gas and oil. The raw oil is further hydrotreated to produce a synthetic crude oil product. Various amounts of fuel gas and char substance are usually produced. [34]

Coal can also be converted to liquid hydrocarbons by using a hydrogenation, or dissolution, process. Coal is slurried with a process-derived oil, heated to temperatures from 700° to 900°F, and allowed to react. A hydrogen makeup atmosphere may be present at pressures from 400 to 4000 psi. The coal dissolves and breaks up into lighter hydrocarbon fragments and gases. Hydrogen can then react with the free radicals in the coal, preventing formation of large amounts of gases or repolymerization to heavy liquids (asphaltenes). The processes also specify various liquid-solid separation schemes to remove the product oil.[15] Table 14-10 gives a brief description and status of liquefaction processes and R&D work.

As might be concluded, hydrogen is very important in the formation of liquid hydrocarbons from coal. It can be reacted directly with a coal slurry, as in a hydrogenation process, or it can be utilized to hydrotreat and upgrade a liquid or a gas produced from the pyrolysis or gasification of coal. Most processes can produce a high-quality crude with low sulfur and nitrogen contents; however, the syncrudes are more aromatic than conventional petroleum ones and will require more severe refining (i.e., hydrocracking). [14] The syncrudes typically have a specific gravity of between 15° and 30° API, a sulfur content of 0.1 to 0.2 weight percent, and a nitrogen content of 0.5 to 0.7 weight percent.

In calculating the hydrogen requirements for the processes it became apparent that, in general, production of liquids from Western U.S. coal requires more hydrogen than production from Eastern coal. It is assumed that the higher oxygen content of the Western coal is responsible for this difference, with hydrogen consumed in removing the oxygen as water. [37] Throughout this section, then, calculations are based on processing Western coals (high volatile C bituminous through lignitic). [9] In the manufacturing of hydrocarbon liquids there is concomitant fuel gas production, the proportion of which varies with each process. In performing calculations of hydrogen requirements, the number of liquid volumes produced was used as a basis

Table 14-10. COAL-TO-LIQUID HYDROCARBONS PROCESSES

Process	Reactor Conditions	Hydrogen Production Method	R&D Status
Pyrolysis			
COED[29]	4 pyrolysis zones of varying temperatures (600°-1500°F) 6-10 psi	Reform fuel gas from process, work underway to gasify char	36 tons of coal/day pilot plant in operation since 1970
Garrett[15]	1600°F, 50 psi	None specified	1/2 ton of coal/day pilot plant in operation since 1973
TOSCOAL[15]	800°-970°F, atmospheric pressure	None specified	25 tons of coal/day pilot plant in operation
Hydrogenation			
Consol Synthetic Fuel[24, 25]	Noncatalytic extraction with hydrogen-donating solvent at 750°F, 150 psi; catalytic hydrogenation of solvent at 800°F, 3500 psi, ebullating staged-bed reactor	Gasify extract residue plus raw coal	20 tons of coal/day pilot plant in limited operation since 1967
Gulf Catalytic Coal Liquids[15]	800°F, 3000 psi, fixed bed catalytic reactor	Steam reform the light hydrocarbons produced	120 pounds of coal/day pilot unit in operation
H-COAL[15]	850°F, 3000 psi, ebullating catalytic reactor	Gasify raw coal and filter cake	3 tons of coal/day pilot plant in operation
SRC[2, 26]	800°-900°F, 1000-2000 psi	Separate onsite coal gasification	6 tons of coal/day pilot plant in operation at Wilsonville, Alabama; 50 tons/day pilot plant recently completed in Tacoma, Washington
Synthoil[39]	800°F, 2000-4000 psi, fixed-bed catalytic reactor	Separate onsite coal gasification	1/2 ton of coal/day pilot plant in operation, 10 tons/day pilot plant in design stage
Gasification			
Fischer-Tropsch[13]	430°-625°F, 330-360 psi, fixed and fluidized catalytic-bed reactors	Reform internally produced methane	Commercial plant completed in 1955 at Sasolburg, South Africa

(i.e., SCF of hydrogen per barrel of liquids). Additional process hydrogen that could be used to synthesize SNG is not included. This factor, in addition to the different product slate of each method, makes direct comparisons of the processes difficult and possibly misleading when relying solely on hydrogen-consumption information.

Pyrolysis processes can use outside hydrogen in hydrotreating the recovered oil and can eliminate internal production of hydrogen from steam reforming of the coproduct synthesis gas. A plant conceptualized as producing 27,300 barrels of syncrude requires 136 X 10^6 SCF of hydrogen; thus hydrogen usage is 5000 SCF/bbl of syncrude produced.[32] More gas from the modified process is now available for use as fuel or feed for an SNG production system.

Selective hydrogenation involves formation of liquid hydrocarbons under more severe conditions of pressure, usually in the presence of a catalyst. Outside hydrogen can be directly added to the hydrogenation reactor or solvent regenerator to fulfill the hydrogen requirement. Using the H-COAL Process, 8500 SCF of hydrogen/bbl of syncrude are required to produce a high-quality crude of 32°API gravity that contains 0.1% nitrogen and 0.1% sulfur.[14] The Synthoil Process uses 6000 SCF of hydrogen/bbl of fuel oil (containing 0.2% sulfur) produced.[37] Use of outside hydrogen in these processes eliminates the need for production of hydrogen by gasification of various combinations of solid extract, char, or raw coal. Use of high-purity, pressurized hydrogen, as would be available from a pipeline, is very amenable to catalytic hydrogenation processes, which require a minimum hydrogen partial pressure of 1000 psi.

Hydrocarbon liquids can also be made by first gasifying the coal to a synthesis gas and then catalytically recombining the carbon oxides with hydrogen to make hydrocarbon liquids. This is commercially embodied in the Fischer-Tropsch Process. Production of 4000 bbls of light oils/day results in a hydrogen deficit of 6 million SCF. Currently this is mostly compensated for by reforming the product methane. Outside hydrogen usage could be about 1500 SCF/bbl. (See Table 4-11.) If outside hydrogen is used, methane need not be reformed, so more SNG is available from the process. Tar, tar oil, and naphtha produced in the gasifier could be partially oxidized to provide the carbon monoxide required for liquid synthesis.

Table 14-11. TYPICAL MATERIAL BALANCE OF GASEOUS STREAMS IN A FISCHER-TROPSCH FLUIDIZED-BED REACTOR[13] (4000 bbl/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	25	2
Hydrogen	60	45
Carbon Dioxide	5	12
Methane	9	35
Other	1	6
Total	100	100
10^6 SCF/Day	146	55

Hydrogen Consumed in Reactor —

$0.60 \times 146 \times 10^6$ SCF/Day (In) $- 0.45 \times 55 \times 10^6$ SCF/Day (Out)
$= 63 \times 10^6$ SCF/Day

Amount of Hydrogen Available From Lurgi Gasifier —

$0.59 \times 96 \times 10^6$ SCF/Day of Synthesis Gas $= 57 \times 10^6$ SCF/Day

Hydrogen Deficiency Requirements —

$63 \times 10^6 - 57 \times 10^6 = 6 \times 10^6$ SCF/Day (Currently Supplied by Steam Reforming Internally Produced Methane)

Theoretical Volumetric Ratio of Hydrogen to Product —

$$6 \times 10^6 \text{ SCF} \div 4 \times 10^3 \text{ bbl} = 1500 \text{ SCF/bbl}$$

Oil Shale Conversion to Liquid and Gaseous Hydrocarbons

It is anticipated that oil shale will make a significant contribution to the U.S. fossil fuel supply in the foreseeable future. Kerogen and bitumen containing rock can be processed to release most of the carbonaceous matter that can be further treated to synthesize conventional refinery products.[31] Perhaps the key step in shale oil production is the retorting of the previously mined and sized shale. Heat is used to decompose the organic materials to water, carbon dioxide, liquid and gaseous hydrocarbons, and carbonaceous residue, which adheres to the spent shale. Conventional retorting is done at approximately 900 ^{0}F.[1] Currently conceived retorting processes, which generally differ in their methods of heat generation and transfer, are summarized in Table 14-12.

A hydroretorting scheme is now under development at the Institute of Gas Technology (IGT) in which oil and gas are produced from shale by heating the shale in a hydrogen atmosphere. Testing indicates that a higher percentage of organic carbon is recovered with the use of hydrogen than with an inert atmosphere (98% versus 77% recovery). The additional hydrogen required for the process can be supplied by gasifying the heavy-oil fraction produced.[28]

The gas produced concurrently with the oil in the retorting step could also be used as a valuable coproduct. It is composed of carbon dioxide, hydrogen, carbon monoxide, LP gases, and hydrogen sulfide and is about 15 weight percent of the product yield.[24] After hydrogen sulfide removal, it could be used as an onsite fuel gas for process heat or electric power generation or could be further treated to make substitute natural gas.

The principal liquid product obtained from the retorting process is of a rather high specific gravity and nitrogen content. Consequently, it must be treated in some way before it can be refined to more valuable products. Catalytic hydrotreating is the preferred means of upgrading the raw oil to a synthetic crude.[16]

Currently conceived retorting schemes for the production of gases and liquids have no external hydrogen requirements. Conceptually, some hydrogen could be used in the production of SNG from fuel gas. Most retorts are designed to produce a preponderance of liquids that would be transported elsewhere for refining to marketable products. An outside source of hydrogen

Table 14-12. PROCESSES FOR OIL SHALE RETORTING TO GASEOUS AND LIQUID HYDROCARBONS[31]

Process	Retort Description	R&D Status
Development Engineering	Internal combustion of carbonaceous residue with air, countercurrent gas-shale flow	500 tons of shale/day testing completed
Gas Combustion	Internal combustion of gas and carbon residue, four functional zones	360 tons of shale/day testing completed
IGT	1200°-1400°F, 125-500 psi, three zones with externally heated hydrogen reaction atmosphere	1 ton of shale/hr pilot development unit nearly complete, laboratory thermobalance work continuing[8]
Lurgi-Ruhrgas	Externally heated sand, coke, or spent shale used in sealed, screw-type retort	12 tons of shale/day pilot plant operated (now dismantled)
Occidental	In-situ retorting of unmined shale by combusting with air	Field testing as of 1972
Petrosix	Externally heated gas retorts shale	2200 tons of shale/day semiworks plant in operation
TOSCO II	Externally heated spheres raise shale temperatures to 900°F at a pressured slightly above atmospheric	1100 tons of shale/day semiworks plant in operation
Union Oil	Internal gas combustion of shale fed into bottom of retort with a "rock pump"	Prototype work since 1950's on 1200 tons of shale/day unit

could not be easily integrated with proposed retorting schemes without more developmental work. A hydroretorting scheme under development at IGT would use an outside source of hydrogen in the retorting of liquids and gases from oil shale. The hydrogen consumption is 1900 SCF/bbl of oil produced and 1200 SCF/thousand SCF of SNG produced.[35]

The raw, retorted shale oil is usually too viscous for easy handling (i.e., by pipeline or tank car), so further treatment is required to facilitate transportation for refining. The raw oil also contains more sulfur and nitrogen than conventional refining catalysts can withstand. A hydroprocessing step is most convenient for upgrading the shale oil to a more typical crude.[14] About 1300 SCF of hydrogen would be consumed in producing one barrel of high-quality syncrude (36 °API, 0.02% sulfur, 0.6% nitrogen, and no fraction boiling over 950 °F).[11] The oil can also be made less viscous by using a coking or "vis-breaking" operation at the retort site, but this would result in more severe refining conditions and would not significantly reduce the overall hydrogen requirements.[23]

The hydrogen requirements for the synthetic fuel processes are summarized in Table 14-13.

Table 14-13. TYPICAL HYDROGEN REQUIREMENTS FOR PRODUCTION OF SYNTHETIC FUELS

Process	Amount of Hydrogen/Unit of Product
Coal to SNG	
Lurgi single-stage gasification	970 SCF/1000 SCF
Multistage hydrogasifiers	1100-1500 SCF/1000 SCF
Coal to Methanol	42,000 SCF/ton
Coal to Syncrude	
Pyrolysis	5000 SCF/bbl of syncrude
Hydrogenation	6000-8500 SCF/bbl of syncrude
Gasification (Fischer-Tropsch)	1500 SCF/bbl of light oil
Oil Shale to Syncrude	
Conventional retort	1300 SCF/bbl of syncrude
Hydrogasifying retort	1900 SCF/bbl of syncrude

The Economics of Outside-Hydrogen Utilization

The use of outside hydrogen requires process and equipment modifications that generally simplify the production of synthetic fuels. Most of the reduction in complexity is due to the elimination of the onsite hydrogen-production facility itself. The deletion of a shift reactor or special gasifier obviously reduces capital requirements, maintenance costs, and process utility requirements. An external hydrogen supply relieves the synfuel processes from having to operate at conditions to optimally make both product and feed for hydrogen production.

Because synthetic fuels processes can be greatly simplified by the use of outside hydrogen, the economics of outside-hydrogen utilization are not straightforward. A preliminary economic analysis was performed that compared the synthetic product costs for internal and external sources of hydrogen. The analysis was based on data from Volume III of "Alternative Fuels for Automotive Transportation — a Feasibility Study."[24] An item-by-item comparison of process components was made for three all-coal synfuel process plants and three coal-plus-hydrogen plants to determine the capital investment and operating cost for SNG, methanol, and liquid-hydrocarbon production. Outside hydrogen was treated as a purchased utility for each of the process families. Costs are based on constant 1973 dollars, allowing product-price determinations for comparison of synthetic-fuel processes involving internal and external hydrogen production. A discounted cash flow (DCF) method was used to determine costs, and economic values were set as follows:

- A 25-year plant life expectancy
- Depreciation calculated on a 16-year, sum-of-the-digits formula
- 100% equity capital
- A 48% Federal income tax rate
- A 12% DCF rate
- Plant startup costs as expenses in year 0.

Break-even costs for synthetic fuels were estimated by comparing an all-coal process with a coal-plus-hydrogen process (at given coal costs) to determine the hydrogen cost that would result in the same product price

for both systems. We assumed that hydrogen would arrive by pipeline at 1500 psi, because transmission studies have shown that hydrogen can be moved more economically at such pressures.[17] The results are presented in Figure 14-6. Combinations of coal and hydrogen costs above and to the left of the lines indicate that it is economically desirable to utilize outside hydrogen for the processes while values below and to the right indicate that it is economically undesirable.

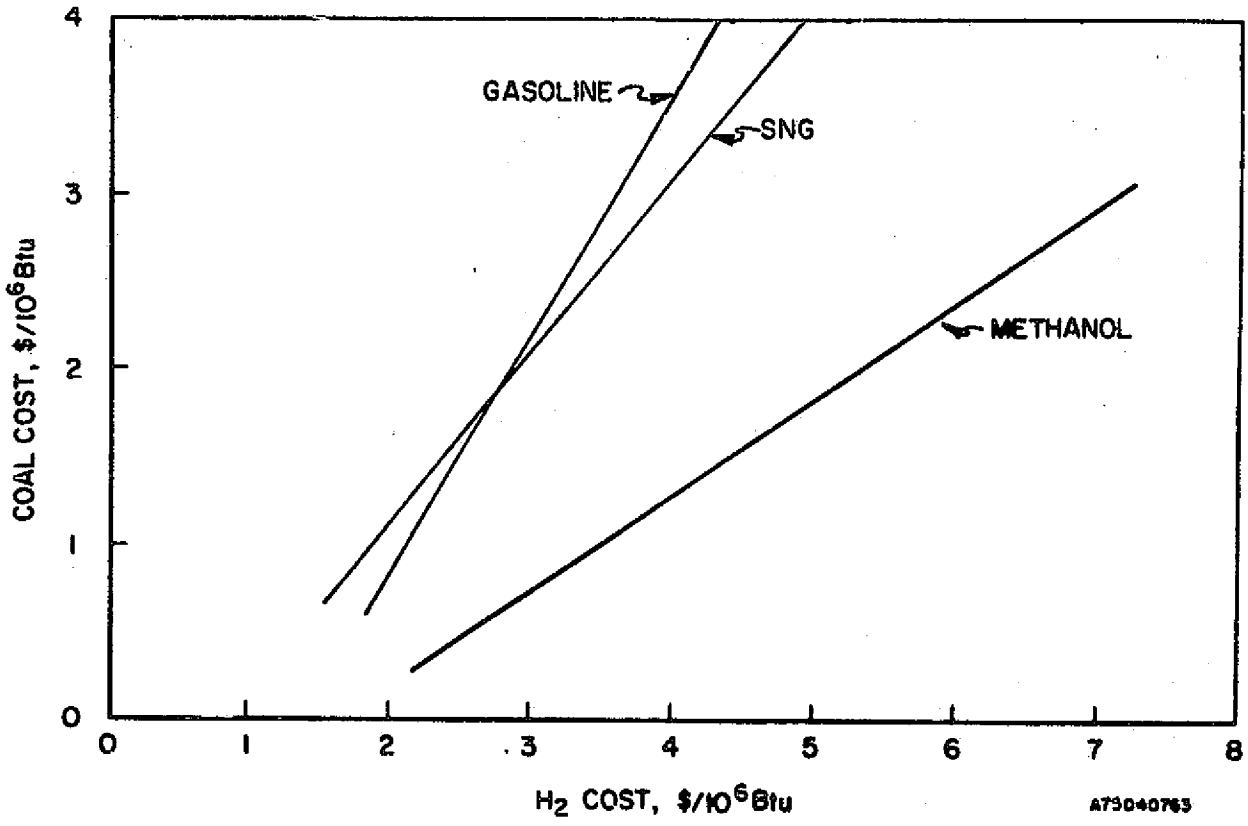

Figure 14-6. BREAK-EVEN COSTS FOR SYNTHETIC-FUELS PRODUCTION FROM COAL AND COAL-PLUS-HYDROGEN PROCESSES

By parametrically varying the cost of coal and hydrogen, it was determined that methanol production favors the use of outside hydrogen at $4.10/million Btu when coal costs exceed $1.15/million Btu. The corresponding methanol price is $115/ton.

For SNG production, a set of raw-materials costs can be determined at which the cost of manufacturing the product is the same, $6.52/1000 SCF, for both conventional and modified processes. The resulting break-even coal cost is $3.20/million Btu, and the hydrogen cost is $4.10/million Btu.

Gasoline can be made from the hydrocarbon product that is made from coal by using the Consol Synthetic Fuel (CSF) Process. Detailed economic information was available for this process using Eastern U.S. coal only. The amount of hydrogen used is on the same order as that used in other processes that consume Western U.S. coal, so an economic comparison of conventional and modified CSF Processes that use Eastern coal should indicate the same trends as a comparison of other coal-to-gasoline processes that use Western coal. In this analysis, the amount of process hydrogen required for the refinery was also included.

No credit was given for by-product coal residue now available from the modified processes. The residue has a sulfur content slightly higher than that of the coal originally fed, so only if low-sulfur coal is used can the residue be marketed (e.g., as a fuel for power generation). The break-even raw-materials costs for synthetic gasoline processes are $3.74/million Btu of coal and $4.10/million Btu of hydrogen. The resulting gasoline product price for both types of processes is $54.52/barrel.

References Cited in This Section

1. Allred, V. C., "Shale Oil Developments: Kinetics of Oil Shale Pyrolysis," Q. Colo. Sch. Mines 62, Golden, Colorado, July 1967.

2. Baldwin, R. M. et al., "The Solvent Refined Coal Process," Chem. Eng. Prog. 71, 70-71 (1975) April.

3. Bodle, W. and Vyas, K., "Clean Fuels From Coal, Introduction to Modern Processes," Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

4. Cannon, J. F., Koppers Co., Inc., private communication of April 30, 1973.

5. Cramer, T., Ed., "HYGAS: a Status Report," Gas Scope No. 28, (1974) Summer.

6. Cromeans, J. S. and Fleming, H. W., "Commercial Experience With Hydrogen Manufacturing Catalyst." Paper presented at the Symposium on Hydrogen Manufacture — Chemistry and Catalytic Technology, Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles, March 28 - April 2, 1971.

7. Farnsworth, J. F. et al., "Production of Gas From Coal by the Koppers-Totzek Process." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

8. Feldkirchner, H. L. and Tarman, P. B., "Hydrogasification of Oil Shale," Project IU-4-7. Chicago: Institute of Gas Technology, March 1975.

9. Fieldner, A. C. et al., U.S. Bur. Mines Bull. 446, 1942.

10. Gasior, S. J. et al., "Fluidized-Bed Gasification of Various Coals," Chem. Eng. Prog. 71, 89-92 (1975) April.

11. Helwig, K. C. et al., "H-Oil Upgrading of Shale Oil Feeds," Q. Colo. Sch. Mines 62, Golden, Colorado, July 1967.

12. Holmgren, J. D. and Salvador, L. A., "Low-Btu Gas From the Westinghouse System," Chem. Eng. Prog. 71, 87-88 (1975) April.

13. Hoogendoorn, J. C., "Experience With Fischer-Tropsch Synthesis at SASOL." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

14. Kant, F. H. et al., "Feasibility Study of Alternative Fuels for Automotive Transportation." Paper EPA-460/3-74-009-b prepared for the U.S. Environmental Protection Agency, Ann Arbor, Michigan. Linden, N.J.: Exxon Research and Engineering Co., 1974.

15. Katz, D. L. et al., "Evaluation of Coal Conversion Processes to Provide Clean Fuels." Paper EPRI 206-0-2 prepared for the Electric Power Research Institute, Palo Alto, California. Ann Arbor, Michigan: University of Michigan, 1974.

16. Kelley, A. E. et al., "Oil Shale Task Group Report," U.S. Energy Outlook, an Initial Appraisal 1971-85, Vol. 2., Summaries of Task Group Reports. Washington, D.C.: National Petroleum Council, 1971.

17. Konopka, A.J. and Wurm, J., "Transmission of Gaseous Hydrogen." Paper presented at the Ninth Intersociety Energy Conversion Engineering Conference, San Francisco, August 26-30, 1974.

18. Landers, J. E., "Review of Methanation Demonstration of Westifield, Scotland." Paper presented at the Sixth Synthetic Pipeline Gas Symposium, Chicago, October 28-30, 1974.

19. LaRosa, P. and McGarvey, R. J., "Fuel Gas From Molten-Iron Coal Gasification." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

20. Lee, A. L., "Methanation for Coal Gasification." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

21. Loeding, J. W. and Tsaros, C. L., "IGT U-Gas™ Process." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

22. Moe, J. M., "SNG From Coal Via the Lurgi Gasification Process." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

23. Montgomery, D. P., "Refining of Pyrolytic Shale Oil," Ind. Eng. Chem. Pro. Res. Dev. 7, 274-82 (1968) December.

24. Pangborn, J. B. and Gillis, J. C., "Alternative Fuels for Automotive Transportation – a Feasibility Study." Paper EPA-460/3-74-012-C prepared for the U.S. Environmental Protection Agency, Ann Arbor, Michigan. Chicago: Institute of Gas Technology, 1974.

25. Phinney, J. A., "Coal Liquefaction at the Pilot Plant Level," Chem. Eng. Prog. 71, 65-67 (1975) April.

26. Schmid, B. K., "Status of the SRC Project," Chem. Eng. Prog. 71, 75-78 (1975) April.

27. Schora, F. C. et al., "The HYGAS Process." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

28. Schora, F. C. et al., "Shale Gasification Under Study," Hydrocarbon Process. 53, 89-91 (1974) April.

29. Scotti, L. J. et al., "The Project COED Pilot Plant," Chem. Eng. Prog. 71, 61-62 (1975) April.

30. Seay, G., Ed., "Summary of High-Btu Gasification R&D Projects," Am. Gas Assoc. Gas Supply Rev. 3. Chicago: Institute of Gas Technology, 1975 May.

31. "Shale Oil Process Choices," Chem. Eng. 81, 66-69 (1974) May 13.

32. Shearer, H. A., "COED Process Plus Char Gasification," Chem. Eng. Prog. 69, 43-49 (1973) March.

33. Strelzoff, S. and Pan, L. C., Synthetic Ammonia, New York: Chemical Construction Corp., n. d.

34. Tek, M. R., "Synthetic Gas and Liquid Fuels From Coal." Paper presented at the 49th Annual Fall Meeting of the Society of Petroleum Engineers of AIME, Houston, October 6-9, 1974.

35. Tsaros, C. L., Institute of Gas Technology, private communication of May 2, 1975.

36. Tsaros, C. L. et al., "Process Design and Cost Estimate for Production of 266 Million SCF per Day of Pipeline Gas by the Hydrogasification of Bituminous Coal – Hydrogen by the Steam-Iron Process," Am. Gas Assoc. Project IU-4-1, OCR Contract No. 14-01-001-381. Chicago: Institute of Gas Technology, 1966.

37. Yavorsky, P. M., "Synthoil Process Converts Coal Into Clean Fuel Oil." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

38. Yavorsky, P. M., "The Hydrane Process." Paper presented at the Clean Fuels From Coal Symposium, Institute of Gas Technology, Chicago, September 10-14, 1973.

39. Yavorsky, P. M. et al., "The Synthoil Process," Chem. Eng. Prog. 71, 79-80 (1975) April.

15. RESEARCH AND DEVELOPMENT RECOMMENDATIONS

From the results of this study, it is clear that there are no major technical reasons for hydrogen not becoming a key component of the future U.S. energy system. However, during the course of this study we found numerous instances in which the ultimate potential of the hydrogen-energy system was unclear because some elements had not been sufficiently developed. Many technologies that are still only conceptualizations or laboratory-scale projects could significantly lower the delivered cost of hydrogen or increase its utility. In this section of the report, we will develop a list of research and development projects that are intended to develop branches of hydrogen-related technology, with the aim of eventually introducing hydrogen on a large scale. If these programs are to be of maximum benefit, they should be completed within the next 5 years.

Production of Hydrogen

This study did not uncover any revolutionary hydrogen-production process that would completely eclipse present-day or contemplated processes. On the other hand, we did find that developmental projects could reduce costs and raise efficiency in established hydrogen-production processes (e.g., electrolysis and coal gasification), could bring advanced processes (e.g., thermochemical production) out of the laboratory, and could establish the feasibility of processes that are currently only concepts (e.g., photosynthesis and those processes based on thermonuclear fusion).

Electrolysis

Research is needed on all aspects of electrolysis. Catalysis, electrode structure, and electrode materials should be investigated. New separators and electrolytes should be developed, and the possibility of better cell design and better power-conditioning equipment should be looked into. Due to experience gained in the development of fuel cells, which are very similar to electrolyzers, some desirable directions for research on electrolyzers are obvious. Because the electrolyzer industry alone cannot afford to carry out the necessary research, this research, conducted on both alkaline and ion-exchange cells, should be supported by either the Federal Government or the potential users of hydrogen.

This support should be divided into that for basic research on electrode structure and gas evolution and that for cell R&D on other topics. Funding for basic research programs should be from $50,000 to $100,000/year. Cell R&D will be more expensive to carry out and should be funded at between $500,000 and $1,000,000 annually. An electrolyzer that operates at about 1.5 volts (a thermal efficiency of almost 100%) and at a current density of about 500 A/sq ft in a piece of equipment with a total capital cost of between $50 and $100/kW input is a reasonable research objective.

For reasons that were pointed out earlier in this report, we recommend that no research on the electrolysis of impure water be funded.

Often, possibly misleading comparisons are made between optimized nuclear thermochemical systems and nonoptimal nuclear electrolytic systems. A short, perhaps 2-year, study to determine the cost effectiveness and efficiency of a nuclear-powered electrolysis plant, specifically designed for hydrogen production, is needed. Such a study would cost between $50,000 and $100,000/year. A program of this type has been funded as a continuance of this program.

The production of hydrogen by thermal-electric or photovoltaic conversion of solar energy should also be investigated. A 3 year, conceptual-design study could be conducted, at the same level as the optimized nuclear-electrolytic study, to provide the technical and economic data needed for comparisons with other processes.

Coal Gasification

The practicality of hydrogen production by the gasification of coal should be further assessed to determine not only how this production method compares with nonfossil-based processes, but also how it compares with traditional methane reforming and partial oxidation of fuel oil. Such information would be of great interest to industries that, because of natural gas curtailments, may soon be faced with the problem of finding an alternative hydrogen source. Several studies should be performed in order to examine the numerous possible gasification schemes. Approximately $100,000 to $200,000/year would be required per study.

Thermochemical Methods

The development of a successful thermochemical water-splitting process could be the key to the introduction of hydrogen as a fuel. It seems likely that thermochemical hydrogen production could significantly lower the price of nuclear-based hydrogen. Three or four laboratory projects should be funded at from $750,000 to $1,000,000/year until a good cycle emerges. Efforts should be directed toward identifying suitable energy sources besides HTGR's and developing more efficient cycles that operate with noncorrosive reactants. These programs eventually should develop kinetic data and heat and material requirements for the most promising cycles.

Application of Controlled Thermonuclear Fusion

A short feasibility study, about 2 years in duration, at a cost of from $50,000 to $75,000 is needed to assess the possibility of water splitting by ultraviolet light beams. Further R&D should be recommended if the concept shows merit.

Photosynthesis

Photosynthetic hydrogen production is very promising for the long term, and appropriate research strategy would seem to be basic and long-range, as well as exploratory shorter range, research in the areas in which breakthroughs are expected or required. The probability of success will be proportional to the number of individual creative scientists (or scientific groups) involved, rather than to the total manpower or money invested. Several independently sponsored groups, funded in relatively small increments (e.g., from $50,000 to $200,000/yr), should maintain close communication to advance conceptual developments. Suggestions for specific projects would best be made by the investigators themselves and evaluated by peer review (with creative feedback). The interdisciplinary nature of the task should be recognized; and cooperation, as well as communication, among representatives from the various disciplines should be encouraged. In particular, colloid catalysis, electrochemistry, and ligand field theory, together with engineering theory, may be helpful. The long-range nature of the problem should be recognized, and funding should be continuous throughout the next 5 years.

Table 15-1 is a summary of the recommended hydrogen-production R&D projects.

Table 15-1. HYDROGEN PRODUCTION – GOVERNMENT RESEARCH AND DEVELOPMENT RECOMMENDATIONS, 1975-1980

Program Title	Years Pursued	Average Annual Funding Level per Program, $1000	Number of Programs	Total 5-Year Period Funding, $1000	Project Description	Project Goals
Electrolysis of Water (Basic Research)	Cont.*	50-100	1-3	250-1,500	Basic work on electrode structure and the mechanism of gas evolution	Achieve 1.5 volts at 500 amp/sq ft; $50-$100/kW capital cost (cell and ancillaries) with 750-1000 psi delivery. Derive less expensive catalytically active electrodes
Electrolysis of Water (Cell R&D)	Cont.*	500-1000	1-3	2,500-15,000	Parallel programs on alkaline and ion-exchange-type cells	Increase operating temperatures and pressures; less dependence on noble-metal catalysts
Integrated Nuclear-Electrolytic Production Facility (Concept Study)	2	50-100	2	200-400	Conceptual engineering design and preliminary economic assessment of dedicated nuclear facility	Provide technical and cost information for advanced production facility planning; provide equitable "referee" concept for nuclear-thermochemical facility evaluation; evaluate land- and offshore-based options
Solar Hydrogen-Production Facility(Concept Studies)	3	50-100	3	450-900	Conceptual engineering design and preliminary economic assessment of solar hydrogen plant	Provide technical and cost information for advanced production facility planning; determine relative role of thermal-electric and photovoltaic energy-conversion modes; evaluate land- and ocean-based options
Hydrogen From Coal (Applications Studies)	2	100-200	2	400-800	Small programs to explore new technology (related to making hydrogen from coal) that is not being developed by other coal-gasification research	Identify ways of making hydrogen from coal that are better than those being developed as part of coal-to-methane projects; if this goal should be reached, large sums ($20-$30 million) would be needed for process development.
Thermochemical Water Splitting (Laboratory Research and Studies)	Cont.*	750-1000	3-4	11,250-20,000	Chemical-cycle derivation and thermodynamic evaluation; laboratory testing of reaction steps; heat-source/cycle interface study; detailed efficiency and flowsheet analysis and economics assessment	Find more efficient cycles with less corrosive materials; determine operating conditions and measure kinetics; define heat requirements and materials; assess overall practicability and economics; determine suitable energy sources other than HTGR's
Controlled Thermonuclear Fusion Production (Feasibility Assessment)	2	50-75	1	100-150	Theoretical feasibility study of the applicability of fusion to hydrogen production	Assess practicability and recommend R&D as appropriate. (Large sums will be needed if these concepts show promise.)
Photosynthetic Production (Basic Research)	Cont.*	50-200	5-7	1,250-7,000	Parallel research on identification of photosynthetic water-splitting mechanisms and electron transport in both "natural" and "synthetic" systems	Determine general chemistry of photosynthetic steps; demonstrate "synthetic" photosynthetic approaches; modify steps for hydrogen production and determine stabilization techniques

* Continuous support over a 5-year period recommended.

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Delivery and Storage of Hydrogen

At present, there is no widespread system for the transmission and distribution of hydrogen. The small-scale distribution systems that have been built (like those of NASA) are probably unsuitable as models for a large-scale system, which must be relatively inexpensive. Despite the success of these small systems, there are numerous technical questions about hydrogen distribution that remain unanswered and possibly some technical problems that remain unsolved.

Pipeline-Materials Compatibility Evaluation

Whether hydrogen can be transmitted through existing natural gas pipelines or whether new pipelines will be needed because of materials problems has yet to be resolved. The materials studies conducted thus far have identified potential problem areas, but have not provided any definite answers. This question should be answered soon because it has significant bearing on how and when hydrogen could be used as a "universal fuel." More than one study of the problem should be funded at approximately $300,000/yr, and results would probably be available in 2 years. These studies should investigate hydrogen-related problems such as loss of metal ductility, hydrogen stress cracking, and hydrogen-environment embrittlement in pipeline steels. If problems exist, possible solutions should be evaluated.

Hydrogen-Transmission-System Experimental Feasibility Studies

If hydrogen-environment embrittlement in pipeline steels proves to be a manageable problem, an investigation into the behavior of other gas-transmission-system equipment with hydrogen should be undertaken. The equipment should be tested under anticipated operating conditions, thereby identifying any furhter complications. Concurrently, engineering studies should be undertaken to determine the economic feasibility of hydrogen transmission. We estimate that the cost of the experimental equipment-compatability study would be $300,000/yr and that the design and costing study might require as much as $100,000/yr for about 3 years. A large-scale system test costing $5,000,000 would follow these preliminary studies.

Pipeline Compressor Evaluation

Early studies of hydrogen pipelining show great divergence on the subject of hydrogen compressors and the units that drive them. A small-scale study

(approximately $100,000/yr for 2 years) could determine the best compressor-prime mover combination and could provide data for the transmission-system cost study described above.

Underground and Hydride Storage of Hydrogen

Underground cavities will allow for inexpensive hydrogen storage, if such a method of storage is possible. Preliminary feasibility studies (both theoretical and experimental) on the effects of the presence of hydrogen on the mechanisms of gas sealing should be undertaken. Two 2-year studies, costing $75,000/yr, should be adequate. Later, far larger sums will be needed for full-scale field testing.

Storing hydrogen in the form of metal hydrides may be important not only for mobile applications, but also for electric-utility peak shaving and as an alternative to underground or line-peak storage. New alloys are still being identified, and support for several laboratory efforts should continue at a minimum of $200,000/yr for the next 5 years. New alloys should be lower in weight and in volume per weight of hydrogen stored and should dissociate at practical temperatures. The specific applications will determine the optimum characteristics, but low cost will be important in almost all.

Behavior of Hydrogen in Gas-Distribution Equipment

There is a dearth of information on the behavior of hydrogen in existing natural gas distribution lines and related hardware. Experimental studies should be conducted to determine the problems encountered with the meters, regulators, and various nonferrous pipe materials in distribution systems. A study of this sort could take several years at an average cost of $300,000/yr.

Improved Cryogenic Systems

Although the amount of energy lost in hydrogen liquefaction is large because of current liquefaction technology, there may be cases in which hydrogen liquefaction is the only practical storage alternative.

Large-scale, liquid-hydrogen facilities (for both processing and storage) are not cheap, but perhaps need not be as expensive as they are now. Engineering studies directed toward the design of economical, very large-scale liquid-hydrogen tankage should be undertaken by prospective equipment manu-

facturers. Integrated storage schemes that allow utilization of boil-off gases would be worthwhile.

The possibility of liquid-hydrogen transmission should also be studied, especially in the context of integrating it with superconducting or "cryoresistive" cables for electric-power transmission. The advantage of being able to combine it with electric-power transmission may make the transmission of liquid hydrogen more attractive than has been the case with liquid natural gas. There seems to be little urgency for this work because cryoresistive-transmission technology has been developed to only an early stage thus far. Studies on cryogenic systems should be funded continuously at $75,000/yr.

Hydrogen Odorants and Illuminants

Because hydrogen gas is odorless and its combustion is nonluminous, odorants and illuminants will have to be selected and added to the gas. These substances should be as pollution free in combustion as possible and should not impair the operation of catalytic devices. (Methylmercaptans, the odorants added to natural gas streams, are sulfur-containing compounds that might poison the platinum catalysts used in some experimental burners.) The identification of odorants and illuminants is not a pressing task, but it should be undertaken within the next 5 years. The effort need not be large: $50,000 to $75,000/yr for two programs (one on odorants and one on illuminants, with intercommunication) over a 2-year period should produce the desired results.

Table 15-2 is a summary of the recommended hydrogen-delivery R&D programs.

Utilization of Hydrogen

Studies of Hydrogen Utilization in Industry

Our study has identified at least five large industrial processes that are potential users of hydrogen. These are 1) direct reduction of iron ores, 2) ammonia synthesis, 3) methanol synthesis, 4) process-steam generation, and 5) production of synthetic fuels from coal. Although these markets for feedstock hydrogen are not as large as the market for gaseous fuel, they deserve special consideration because their economics may allow them to use

Table 15-2. HYDROGEN-DELIVERY RESEARCH AND DEVELOPMENT RECOMMENDATIONS, 1975-1980

Project Title	Years Pursued	Average Annual Funding Level per Program $1000	Number of Programs	Total 5-Year Period Funding, $1000	Project Description	Project Goals
Pipeline-Materials Compatibility Evaluation (Materials Investigation)	2	300	2	1200	Experimentally assess any hydrogen embrittlement problems encountered when transmitting hydrogen through present-day natural gas pipelines	If embrittlement problems are found to be serious, large additional programs will be needed to test solutions.
Hydrogen (Gas) Pipeline Design and Costing (Engineering Study)	3	100	1	300	Gaseous-hydrogen transmission system evaluation; to be begun after preliminary studies are completed	Establish optimized hydrogen-pipeline-system characteristics and component requirements; determine transmission economics (related to those of natural gas)
Hydrogen (Gas) Transmission System Experimental Operating Loop (Experimental Feasibility Project)	1	5000	1	5000	Testing of gaseous transmission equipment (compressors, metering devices, etc.) under actual pressures and flow conditions with hydrogen. Program to commence after preliminary studies are done	Evaluate present natural gas transmission equipment under anticipated hydrogen conditions and over extended periods; develop modified and new components and subsystems as required; derive engineering design and operating experience
Pipeline-Compressor Evaluation (Design Study)	2	100	1	200	Selection and design of large hydrogen-pipeline compressors and drives	Determine best compressor type and matched prime mover for large-diameter hydrogen pipelines; document technical specifications and costs
Underground Hydrogen Storage (Feasibility Study)	2	75	2	300	Feasibility assessment of storing gaseous hydrogen underground; one study each on aquifers and mined caverns	Evaluation of suitability of present natural gas techniques for underground storage of hydrogen; estimate quantities of storage in present reservoirs and those potentially developable in the United States; develop economics of underground storage
Metal-Hydrides Storage (Basic Research)	Cont.*	200	1	3000	Search for promising metal hydrides for stationary (and mobile) storage applications	Identify practical materials and evaluate on the basis of developed criteria (heat of formation, dissociation temperature, weight and volume, cost, etc.)
Hydrogen (Gas) Distribution System (Experimental Feasibility Study)	Cont.*	300	1	1500	Testing of gaseous distribution equipment mains, meters, regulators, etc.) under actual pressures and flow conditions with hydrogen	Evaluate present natural gas distribution equipment under realistic hydrogen conditions and over extended periods of time; provide basis for modifying equipment and introducing new equipment; derive engineering design and operating experience
Improved Cryogenic Systems	Cont.*	75	2	750	Assessment of required advancements and initial hardware efforts in cryogenic hydrogen technology	Technological improvements to achieve high efficiencies and low costs; focused studies and preliminary hardware work to advance the technology in a) liquefaction, b) transmission (pipeline and vehicular), and c) storage-container (from small portable to large stationary) application sectors
Hydrogen Odorants and Illuminants	2	50-75	2	200-300	Devising of practical additives to hydrogen to provide for olfactory and visual (flame) warnings to personnel with unwanted side-effects	Provide for several candidate hydrogen odorant and illuminant materials that do not adversely affect catalysts and other exposed materials; demonstrate economic feasibility and practicability in the field

*Continuous support over 5-year period recommended.

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hydrogen that is too expensive to be used as a fuel. Thus, these processes, especially ammonia synthesis, may be the first applications for hydrogen technology – even while new, low-cost methods of hydrogen production are under development.

Feasibility studies, in greater depth than those done in this study, should be conducted to determine the conditions under which it will be economical to use "outside" hydrogen in these processes. Three of the processes (steam production, ammonia synthesis, and methanol synthesis) involve only a moderate amount of new technology, and feasibility studies could be conducted at a cost of from $75,000 to $100,000 per process.

The use of pure hydrogen in the direct reduction of iron ore will, as was discussed in Section 12, require the development of a few new materials-handling techniques. The problems are not serious, but they will require some experimental work. For this reason, feasibility studies on this process should be funded at a higher level, about $150,000/yr for from 1 to 2 years. Multiple efforts would be more likely to produce satisfactory results.

Outside-hydrogen utilization by the future synthetic-fuels industry will also require a more complicated feasibility study. The fundings and time scale should be about the same as that for the direct-reduction process.

Development of Hydrogen-Fueled Appliances

The assessment of the adaptability of present-day appliances to hydrogen fuel, as shown in Section 13, has not really progressed beyond the discussion stage. Nevertheless, any widespread use of hydrogen as a replacement for natural gas will probably require the conversion of many natural gas appliances. Experimental studies to determine what conversion parts and procedures will be necessary should be initiated soon. Two or three such studies at about $250,000/yr should provide answers in from 2 to 4 years.

Very little work has been done on the development of catalytic appliances. These devices exploit the full potential of hydrogen and should be developed if for no other reason than to provide a basis for comparison of hydrogen with other, more developed energy options. Better catalysts (both high and low temperature) and improved burner configurations are needed, and practical prototype appliance models should be developed. Because the work is still in a highly creative stage, multiple efforts (perhaps as many as four)

should be undertaken. The cost of these programs would be from $100,000 to $250,000/yr (depending on the scale of the proposed development), and the projects should continue for the next 5 years.

Besides the across-the-board conversion of all gaseous-fuel equipment in given areas to hydrogen, hydrogen might be used as a gaseous fuel by blending it with natural gas supplies. A study of this possibility should begin immediately and should be continued at $100,000/yr for the next 5 years as the natural gas situation changes.

By-Product Credits

A potential-market study should be initiated immediately on the use and value of the oxygen produced as a by-product in the manufacture of hydrogen.* An economic analysis of long-distance oxygen transmission by pipeline should be included in this study. Studies should be made on an industry-wide basis (perhaps by the government), but the detailed equipment development probably should be performed by existing large-scale oxygen suppliers. We estimate that these studies will cost a total of $100,000/yr for a 2-year period.

The recommended R&D programs on the utilization of hydrogen are summarized in Table 15-3.

* There is the possibility of by-product oxygen use in very rapidly growing markets, such as synthetic-fuels manufacture and sewage treatment, within the next few years.

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Table 15-3. HYDROGEN-UTILIZATION RESEARCH AND DEVELOPMENT RECOMMENDATIONS, 1975-1980

Program Title	Years Pursued	Average Annual Funding Level per Program, $1000	Number of Programs	Total 5-Year Period Funding, $1000	Project Description	Project Goals
Hydrogen for Industrial Process-Steam Generation (Applications Assessment)	2	100	2	400	Evaluation of hydrogen as an energy source for generation of process steam through 1) conventional boilers and 2) hydrogen-oxygen combustion	Determine technical steps for industrial-boiler modification to hydrogen; evolve an optimized (but otherwise conventional) hydrogen-fueled boiler design; provide commercially usable hydrogen-oxygen steam generator system designs; document supporting technology requirements
Optimized Ammonia Production Facility Based on Hydrogen Feedstock (Preliminary Design Study)	1	75	1	75	Preliminary design of an advanced technology, ammonia-synthesis plant based on hydrogen feedstock	Determine design elements of ammonia facility with sufficient costing to evaluate the economic crossover point for a range of natural gas and hydrogen feedstock prices
Optimized Methanol Production Facility Based on Hydrogen Feedstock (Preliminary Design Study)	1	75	1	75	Preliminary design of an advanced-technology, methanol-synthesis plant based on hydrogen feedstock	Determine design elements of methanol facility with sufficient costing to evaluate the economic crossover point for a range of natural gas and hydrogen feedstock prices
Direct Hydrogen Reduction of Metal Ores (Feasibility Study)	1-2	100-150	1-3	100-900	Determination of valued metals whose ore can be directly reduced with hydrogen where feasibility is not in-hand. Process development activity will be pursued in the case of iron/iron ore	Evaluation and improvements of known processes of direct iron-ore reduction with hydrogen (e.g., "H-Iron"); feasibility demonstrations in the case of nonferrous materials; supporting economic studies of commercialization potential
Hydrogen's Role in Synthetic-Fuels Production (Applications Study)	2	100-150	1	100-300	Hydrogen's role as a key constituent in synthetic-fuels production from coal; oil shale characterization and quantification	All significant synfuel-production requirements for hydrogen will be documented; its new and innovative uses will be defined; the potential role of coproduct oxygen will be assessed for synfuels production; economic crossovers will be determined based on coal and shale oil costs and on the process equipment required for onsite hydrogen manufacture versus the cost of externally delivered hydrogen
Conversion of Natural-Gas-Fueled Appliances to Hydrogen (Exploratory Development)	2-3	250	2-4	1000-3000	Investigation of procedures and hardware modifications required for retrofitting of existing fuels	Identify hardware approaches and installation procedures for across-the-board retrofitting; estimate costs for "mods" and for installation
Catalytic Combustion Devices Using Hydrogen (Applied Research)	Cont.*	100-250	2-4	1000-5000	Identification of the best catalysts for low- and high-temperature catalytic combustion; develop suitable configurations for residential, commercial, and industrial burners (including ventless units)	Demonstrate practical catalytic burners for all application sectors that provide acceptable operations, efficiency, and emissions
Hydrogen as a Natural Gas Additive (Study and Planning)	Cont.*	100	1	500	Determination of overall system implications of adding substantial quantities of hydrogen to the natural gas supply as "natural gas stretches"	Determine the ramifications to all facets of the natural gas production, delivery, and utilization areas as progressive amounts of hydrogen are added; identify the cost-optimum maximum hydrogen addition point; develop a long-range plan for this mode of conversion
Oxygen Utilization (Market Study)	2	100	1	200	Investigate new markets for coproduct oxygen	Define and quantify (as a function of price) new and innovative uses for oxygen; assess delivery requirements

*Continuous support over 5-year period recommended.

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